Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Molecular Clustering in Supercritical Solutions

H. D. Cochran[a]; R. -S. Wu[b]; L. L. Lee[b]
[a] Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN [b] School of Chemical Engineering and Materials Science University of Oklahoma, Norman, OK

To cite this Article Cochran, H. D. , Wu, R. -S. and Lee, L. L.(1990) 'Molecular Clustering in Supercritical Solutions', Separation Science and Technology, 25: 13, 2017 — 2031
To link to this Article: DOI: 10.1080/01496399008050441
URL: http://dx.doi.org/10.1080/01496399008050441

SEPARATION SCIENCE AND TECHNOLOGY, 25(13-15), pp. 2017-2031 (1990)

MOLECULAR CLUSTERING IN SUPERCRITICAL SOLUTIONS

H. D. Cochran
Chemical Technology Division
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, TN 37831-6224

R.-S. Wu and L. L. Lee
School of Chemical Engineering
and Materials Science
University of Oklahoma
Norman, OK 73019

ABSTRACT

Molecular explanations have recently identified massive solvent clusters surrounding the dissolved solute as the causative agent of the striking solvent properties of supercritical fluids. Such clusters were first inferred from the large negative values of the solute partial molar volume near the solvent critical point; these clusters were estimated to contain about 100 solvent molecules per solute molecule in excess of the bulk average. Subsequent evidence from visible and ultraviolet absorption and fluorescence spectroscopy and from chemical reaction studies have provided qualitative support for the notion of solvent-solute clusters. Other spectroscopic evidence suggests the formation of solute-solute aggregates, as well, near the solvent critical point. Such structures on a molecular level are describable in terms of the molecular distribution functions. We present results on the size and radial profile of solvent-solute clusters and on solute-solute aggregation for systems representative of typical dilute, attractive, supercritical solutions calculated from integral equation theories. The microstructure of theoretically-predicted dilute, repulsive, supercritical solutions exhibits a deficit of solvent molecules surrounding the solute. Solute partial molar volume and chemical potential are predicted to increase dramatically in such repulsive mixtures as density is increased toward the critical point at slightly supercritical temperatures.

INTRODUCTION

Dilute supercritical solutions are important in separation processes such as supercritical fluid extraction and supercritical fluid chromatography; as we shall suggest later, other separation processes based on the behavior of supercritical solutions may also be

possible. To understand why the behavior takes place an understanding of the mixture on the molecular level is necessary. This understanding will greatly expand our ability to formulate and search for new processes that will perform new separation tasks. We shall review briefly the experimental evidence that the behavior of dilute supercritical solutions near the critical point (CP) of the pure solvent is related to clustering of solvent molecules around solute molecules and aggregation of solute molecules around one another. Theoretical studies of dilute supercritical solutions are consistent with these suggestions of solvent-solute clustering and solute-solute aggregation.

The solute partial molar volume in dilute supercritical solutions as measured by Eckert and coworkers (1,2) became negative and large in magnitude as the CP was approached — *ca.* 100 times the bulk molar volume of the solvent. These results suggested to the authors "...that the solution process represents a disappearance of more than 100 moles of solvent/mole of solute. This suggests some sort of clustering process, perhaps akin to electrostriction about an ion in a protic solvent."

Kim and Johnston (3) observed a shift with solvent density in the frequency of the IR absorption maximum of a solute in a supercritical solvent; that the magnitude of the shift was greater than would have been expected based on the bulk density of the solvent suggested that the local density of solvent molecules surrounding the solute was higher than the bulk density. Thus, Kim and Johnston interpreted their spectroscopic results as independent experimental evidence of solvent-solute clustering in supercritical solutions. Other spectroscopic results (4-11) are consistent with this molecular picture.

Collins *et al.*, (12) studied the disproportionation reaction of toluene over ZSM-5 molecular sieve catalyst in toluene at states which included some near the CP of pure toluene. As the CP was approached the selectivity of the reaction to p-xylene over o- and m-xylene was increased. Clustering of toluene about the p-xylene primary reaction product was invoked to explain these results as follows: if it had not been for the steric shielding due to clustering, the p-xylene would have readily isomerized to an equilibrium mixture of p-, o-, and m-isomers on and within the catalyst particles.

The spectroscopic studies of Brennecke and Eckert (10,11) suggested that another type of molecular clustering may occur in dilute supercritical solutions. For example, they observed the UV fluorescence spectrum of a solution of pyrene in supercritical ethylene near the CP of pure ethylene. At pyrene mole fraction $y_i = 5.5\times10^{-6}$, well below saturation, a broad band appeared at a longer wavelength which was interpreted as the spectrum of excited state pyrene dimers, or excimers, even at this extremely dilute condition. The relative band areas of the pyrene and the excimer spectra indicated that *ca.* 50% of the pyrene molecules exist as excimers. From knowledge of the expected lifetime of pyrene excimers and the kinetics of excimer formation at the prevailing bulk conditions, Brennecke and Eckert concluded that the strong excimer band was evidence of significant solute-solute aggregation in dilute supercritical solutions near the CP of the solvent.

In the following section we shall review the theoretical evidence suggesting solvent-solute clustering and solute-solute aggregation in dilute supercritical solutions. These results offer deeper insight into the factors at a molecular level which influence the

important properties of supercritical solutions. Then, we review the theoretical evidence (13,14) for another type of dilute supercritical solutions — *repulsive* solutions in which the solute is surrounded by a deficit rather than an excess of solvent molecules. Recent experimental evidence (15,16) suggects that Ar, C_2H_4, and Xe may form such repulsive mixtures in supercritical water.

THEORY OF MICROSTRUCTURE IN DILUTE SUPERCRITICAL SOLUTIONS

Kim and Johnston (3) and Debenedetti(17) have interpreted the partial molar volume data of Eckert *et al.*, (1,2) in terms of the isothermal compressibility of the pure solvent and the number of excess solvent molecules in the cluster around each solute molecule; thus, for dilute solutions

$$\Gamma = \rho kT\chi_T - \rho\bar{v}_B \tag{1}$$

where Γ is the cluster size, defined as

$$\Gamma \equiv \rho\, G_{AB} = \rho\int_0^\infty dr\, 4\pi r^2[g_{AB}(r) - 1] \tag{2}$$

The magnitude of Γ was found (17) to be *ca.* 100 excess solvent molecules around each solute molecule near the CP by using an equation of state to estimate the isothermal compressibility of the pure solvent. Kim and Johnston focused on the effects due to the excess solvent molecules at short distances from the solute. The solvent shift in the IR absorbtion frequency is a measure of the local solvent density surrounding a solute molecule; the local solvent density was found to be *ca.* 50% greater than the bulk solvent density based on the spectroscopic results. Debenedetti's (17) analysis was based on Kirkwood-Buff solution theory (18) and expressed in terms of the Kirkwood fluctuation integral

$$G_{\alpha\beta} \equiv \int_0^\infty dr\, 4\pi r^2[g_{\alpha\beta}(r) - 1] \tag{3}$$

or, equivalently, in terms of the fluctuations in the number density of the solvent and the infinitely dilute solute near the CP of the pure solvent. The isothermal compressibility and partial molar volumes may be expressed in terms of the fluctuation integrals. For a binary A—B mixture

$$\rho\bar{v}_B = \frac{\left\{1 + \rho x_A (G_{AA} - G_{AB})\right\}}{\left\{1 + \rho x_A x_B \Delta\right\}} \tag{4}$$

and

$$\rho kT\chi_T = \frac{\left\{1 + \rho x_A G_{AA} + \rho x_B G_{BB} + \rho^2 x_A x_B (G_{AA} G_{BB} - G_{AB}^2)\right\}}{\left\{1 + \rho x_A x_B \Delta\right\}} \tag{5}$$

where

$$\Delta = G_{AA} + G_{BB} - 2G_{AB}. \tag{6}$$

The behavior of the Kirkwood fluctuation integrals for a binary A—B mixture in the vicinity of a CP has been studied previously; for example, see the monograph by Munster (19). Although the correlation range tends to infinity at a CP, the magnitude of the pair correlation function, $g_{\alpha\beta}(r)$, remains always of order unity. Munster (19) shows that G_{AA} and G_{BB} diverge at a CP, but that

$$\lim_{T \to T_c} \left\{ \frac{G_{AB}^2}{(G_{AA} G_{BB})} \right\} = 1. \tag{7}$$

Thus, G_{AB} also tends to infinity at a CP, and the correlation functions and bulk properties are describable by a single correlation function (19). Divergence of the $G_{\alpha\beta}$ may, in fact, be taken as an indicator of criticality (19-21). Thus, while the short-range structure surrounding a solute in supercritical solution increases as the CP is approached, so too does the long-range structure; the growth without limit of the infinite dilution solute partial molar volume and other bulk thermodynamic quantities near the CP of the pure solvent results from increase without bound in the correlation range. There are both short-range and long-range aspects of fluid microstructure of interest and importance.

Many supercritical solutions of experimental or technological importance are quite dilute; we are interested in the implications of the asymptotic condition of infinite dilution in supercritical solutions. Let us simply state Debenedetti's results (17)

$$\lim_{x_B \to 0} \left\{ G_{AA} + G_{BB} - 2G_{AB} \right\} = G_{AA}^0 + G_{BB}^0 - 2G_{AB}^0 = \textit{finite except at a CP} \tag{8}$$

$$\lim_{x_B \to 0} \left\{ G_{BB} - G_{AB} \right\} = G_{BB}^0 - G_{AB}^0 = \textit{finite except at a CP} \tag{9}$$

where here and after the superscript zero indicates the value of the quantity at the limit of infinite solute dilution.

Molecular distribution functions and fluctuation theory then present a rich and appropriate formalism within which to explore the structure and properties of supercritical solutions. Both the short-range microstructure, as probed by spectroscopic techniques, and the long-range growth in the correlation of density fluctuations, as reflected in the growth of the solute partial molar volume, can be described within this framework.

In a series of papers (22-26), Cochran and coworkers presented results calculated from integral equation theories showing the structure of dilute solutions of Lennard-Jones (LJ) particles representative of typical supercritical solutions. Integral equation theories are, of necessity, approximate although the Reference Hypernetted Chain (RHNC) and the Hybrid Mean Spherical Approximation (HMSA) theories have been shown to be accurate within the uncertainty of simulation results for most states and, for moderate-to-low densities, even the Percus-Yevick (PY) theory is accurate (See, for example, (27,28)). The PY theory (and probably the RHNC and HMSA theories which have not been evaluated for this question) exhibit mean-field behavior in the immediate vicinity of a CP and, thus, cannot be accurate in this region; however, the results reported here and

the states of technological interest are sufficiently far from the CP that this limitation is not of concern.

Figure 1 shows the partial molecular volume of naphthalene in supercritical carbon dioxide at reduced temperature $T/T_c = 1.01$; the data are from Eckert *et al.*, (1), and the line is from PY theory with LJ potentials. The satisfactory agreement lends support to the credibility of results that follow which were calculated from this simple model. Figure 2 compares the solvent-solute pair correlation function of a dilute supercritical solution calculated by molecular dynamics (29) with the result from PY theory (for a repulsive mixture, see below). Calculations used the same LJ potential parameters and were at the same state. The simulation results exhibit marked statistical fluctuations beyond the first peak. Again, the satisfactory agreeement lends support to the results from PY theory that follow.

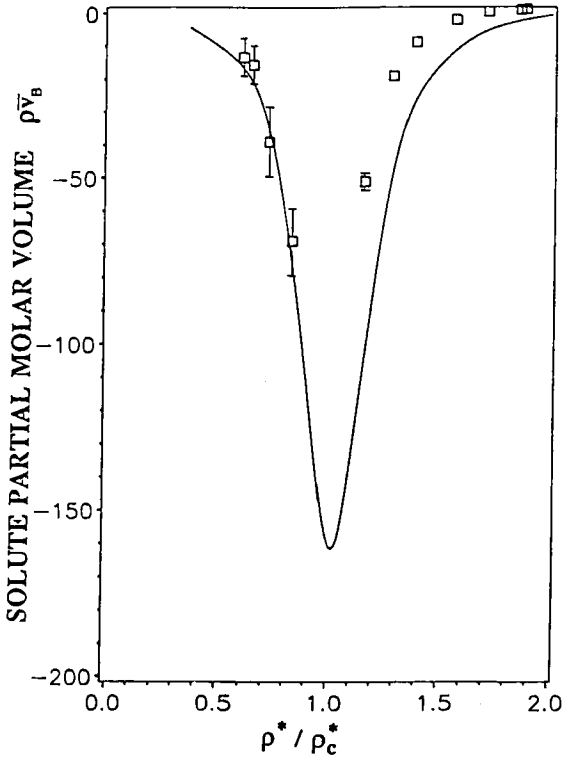


Fig. 1. Partial molar volume of naphthalene in supercritical carbon dioxide *vs.* reduced density at reduced temperature 1.01. Data points from Eckert *et al.* (1); curve calculated from PY theory.

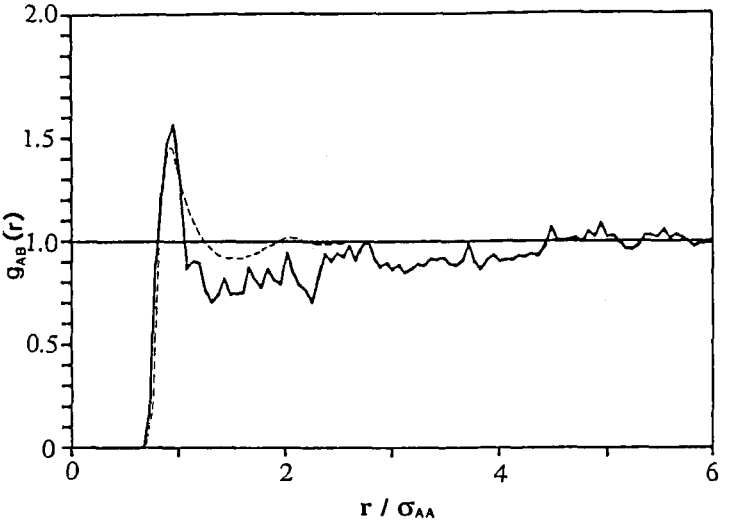
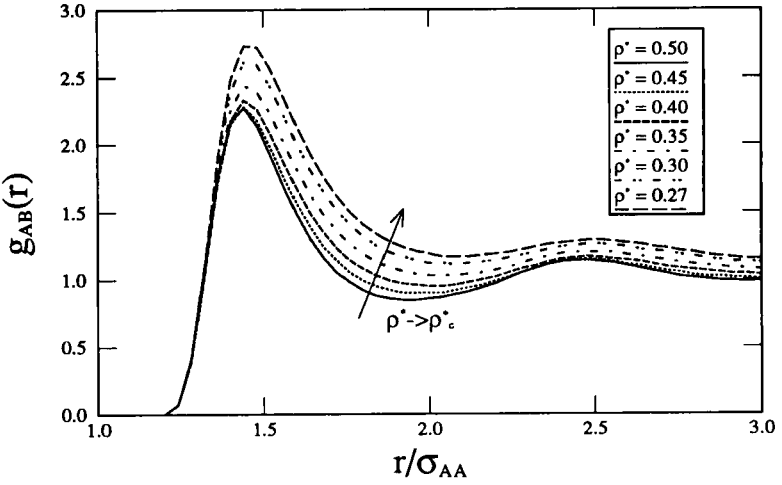


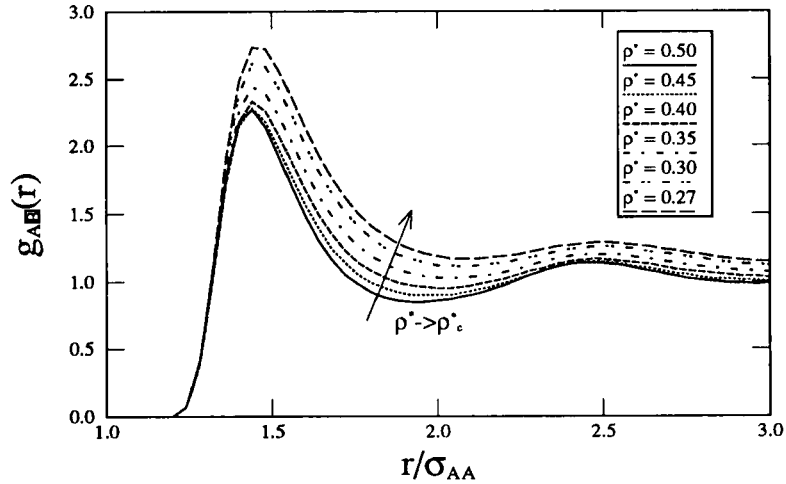
Fig. 2. Solvent-solute pair correlation function for *Ne* in supercritical *Kr* (repulsive mixture). Full line from molecular dynamics (25); dashed line calculated from PY theory.

Figure 3 presents solvent-solvent, solvent-solute, and solute-solute pair correlation functions calculated for a system representative of a typical, dilute supercritical solution near the CP of the solvent. Quantitative examination shows that all three pair correlation functions have long-range tails with $g_{\alpha\beta}>1$ for a dilute solution near the CP of the pure solvent. Figure 3b shows how the solvent-solute pair correlation function grows as the CP of the pure solvent is approached. The growth in the long range tail is responsible for the growth of the partial molar volume, and the increase in the area under the first maximum, for spectroscopic effects. At the same time that the solvent-solute pair correlation function is becoming long-ranged near the CP of the solvent, so also the solute-solute pair correlation function becomes long-ranged. Because of the extreme diluteness of the solute, such solute-solute microstructure has been characterized as aggregation. Figure 3c shows the growth of both short- and long-range structure in the solute-solute pair correlation function as the CP of the pure solvent is approached. This high degree of solute-solute aggregation appears entirely consistent with the spectroscopic results of Brennecke and Eckert (10,11) which indicated a significant amount of excimer formation, even in extremely dilute solutions, as the CP of the solvent is approached.

In addition to typical, attractive, dilute supercritical solutions which form large solvent clusters around each solute molecule near the CP of the solvent, Debenedetti and Mohamed (14) showed that repulsive systems are possible in which a deficit of solvent molecules surrounds each solute molecule. For obvious reasons such systems were said to form dilute, repulsive, supercritical solutions. Biggerstaff and Wood (15,16) have recently measured apparent molar volume and heat capacity for *Ar*, C_2H_4, and *Xe* in supercritical water; these results indicate a deficit of *ca.* 40 water molecules in these



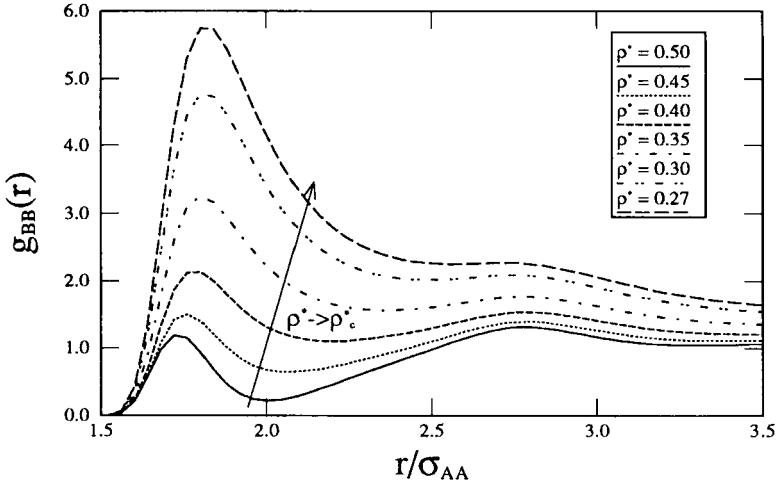
a) Solvent-solvent pair correlation function.



b) Solvent-solute pair correlation function.

Fig. 3. Pair correlation functions for pyrene in supercritical carbon dioxide calculated from PY theory *vs.* reduced density, $\rho^* = \rho\sigma_{AA}^3$, at reduced temperature, $T^* = kT/\varepsilon_{AA} = 1.415$.

(continued)



c) Solute-solute pair correlation function.

Fig. 3. (contd.) Pair correlation functions for pyrene in supercritical carbon dioxide calculated from PY theory *vs.* reduced density, $\rho^* = \rho\sigma_{AA}^3$, at reduced temperature, $T^* = kT/\varepsilon_{AA} = 1.415$.

repulsive mixtures. From Equations (1) and (2) it can be seen that a repulsive system will exist, $\Gamma < 0$, when $(\rho kT\chi_T - \rho\bar{v}_B)$ is negative. Since the first term is always positive, this implies that the partial molar volume should be positive (opposite of the attractive case), and that the magnitude of the partial molar volume term should exceed that of the isothermal compressibility term. Equivalently, a repulsive system will exist when the solvent-solute fluctuation integral is negative, $G_{AB} < 0$. By thermodynamic analysis Debenedetti and Mohamed showed that if a dilute solution of B in A near the CP of A forms a typical attractive solution, then a dilute solution of A in B near the CP of B forms a repulsive solution. For example, since a dilute solution of krypton, *Kr*, in neon, *Ne*, near the CP of *Ne* forms a typical, attractive solution, then a dilute solution of *Ne* in *Kr* near the CP of *Kr* will be a repulsive solution. Indeed, Petsche and Debenedetti (29) performed molecular dynamics simulation studies of LJ mixtures representing both the attractive *Kr* in *Ne* and the repulsive *Ne* in *Kr* systems and the short-range structure of solvent molecules around the solute molecule exhibited just the clustering expected in the attractive system and the rarefaction expected in the repulsive solution. Figure 4, from PY theory, shows the cluster of excess solvent molecules around an attractive solute; also shown is the cluster of solvent molecules around a solute identical to the solvent and the deficit of solvent molecules surrounding a repulsive solute molecule.

Two recent studies (25,26) present results of integral equation calculations for LJ mixtures representative of dilute, repulsive, supercritical solutions. Figure 5 presents

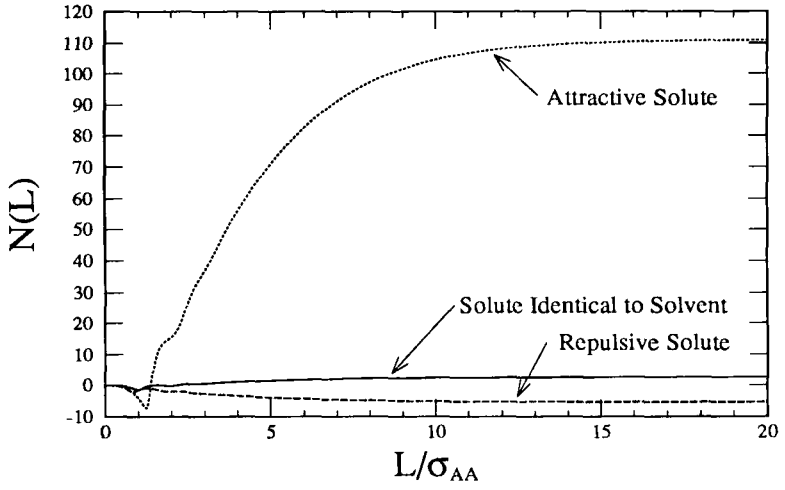


Fig. 4. Cluster size (number of excess solvent molecules surrounding each solute) *vs* reduced distance for an attractive solute, a solute identical to the solvent repulsive, and a repulsive solute calculated from PY theory.

solvent-solute pair correlation functions for such a system as the CP of the pure solvent is approached. Quantitative examination shows that the correlation functions have a long-range tail with $g_{AB}<1$ for a dilute solution near the CP of the pure solvent. Figure 6 presents the deficit in the number of solvent molecules compared with the bulk average within a distance L from a solute molecule for the same states as Figure 5. The positive contributions from the first, second, ... solvation shells and the large negative contribution from the long-range structure are shown in clear perspective. For dilute repulsive supercritical solutions, the negative growth of G_{AB} would result in a dramatic increase in the fugacity and a large positive partial molar volume.

In repulsive systems as in attractive systems, at the same time that the solvent-solute pair correlation function is becoming long-ranged near the CP of the solvent, so also the solute-solute pair correlation function becomes long-ranged. While the solvent-solute microstructure for a repulsive system indicates a deficit of solvent molecules around each solute, the solute-solute structure indicates solute-solute aggregation as in the attractive system. Figure 7 shows the growth of both short- and long-range structure in the solute-solute pair correlation function for the repulsive system as the CP of the pure solvent is approached. Figure 8 shows the solute aggregation surrounding the dilute, repulsive solute for the same states as Figure 7.

Except the recent work by Biggerstaff and Wood (15,16) there is no experimental evidence of the macroscopic effects of the fluid microstructure for a dilute, repulsive system near the CP of the solvent. Theoretical studies, however, appear to be consistent.

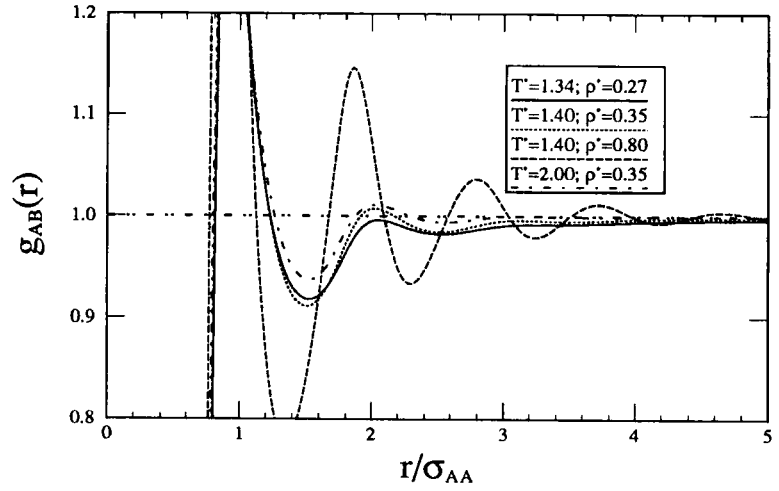


Fig. 5. Solvent-solute pair correlation functions for a repulsive mixture as the CP of the pure solvent is approached calculated from PY theory.

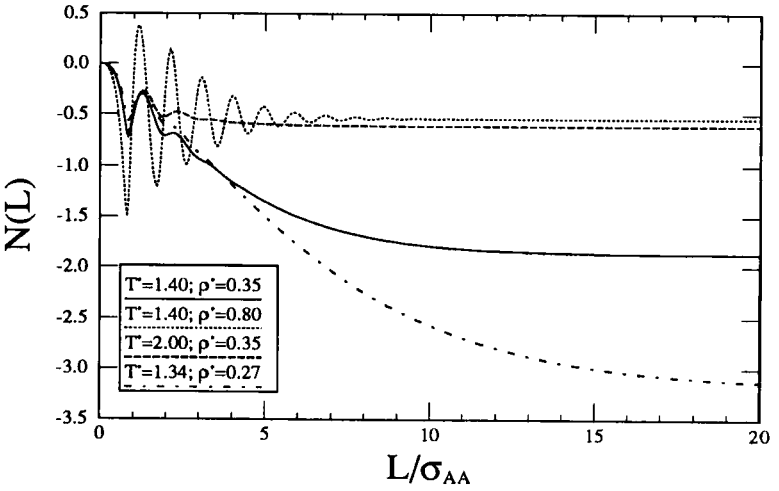


Fig. 6. Solvent-solute cluster size (number of excess solvent molecules surrounding each solute) *vs* reduced distance for a repulsive mixture as the CP of the pure solvent is approached calculated from PY theory.

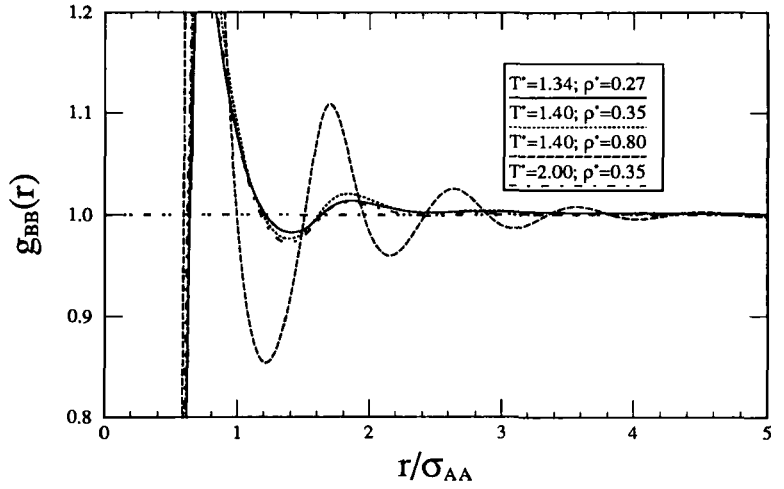


Fig. 7. Solute-solute pair correlation functions for a repulsive mixture as the CP of the pure solvent is approached calculated from PY theory.

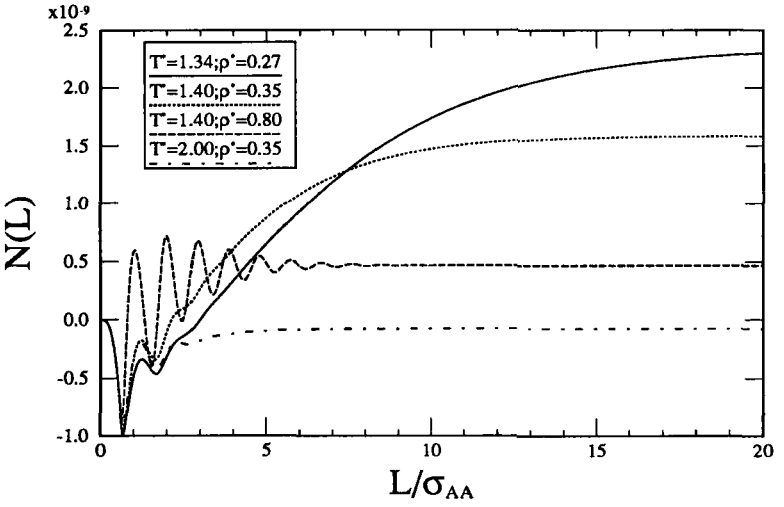


Fig. 8. Solute-solute cluster size (number of excess *solute* molecules surrounding each solute) *vs* reduced distance for a repulsive mixture as the CP of the pure solvent is approached calculated from PY theory. As the bulk concentration of the solute is very dilute, $\rho_B^* = \rho_B \sigma_{AA}^3 = 1\times10^{-9}$, the degree of aggregation shown exceeds twice the bulk concentration.

Figure 2 showed the solute-solvent pair correlation functions for a dilute, repulsive supercritical solution (modeling dilute *Ne* in supercritical *Kr* near the *Kr* CP). The solid line is the result from molecular dynamics simulation (29) and the dotted line is the result from integral equation calculations (26). The repulsive behavior is evident in both results, and the results show reasonable agreement for the short range microstructure where the simulation is accurate. For practical reasons, molecular simulations of supercritical solutions cannot be extended to explore long-range microstructure or solute-solute interactions. These important phenomena may be examined experimentally by neutron scattering studies.

MICROSTRUCTURE EFFECTS ON SEPARATIONS

Through theoretical calculations we have examined the interesting microstructure of dilute solutions near the CP of the solvent for the typical attractive supercritical solutions as well as for the repulsive supercritical solutions that are suggested by theory. Equations 1—6, from Kirkwood-Buff solution theory, relate important bulk properties to the fluid microstructure. Cochran and Lee (30), following work by Debenedetti and Kumar (31), showed that the concentration dependence of the fugacity coefficient of a solute B, ϕ_B, can be calculated from its value at infinite dilution, ϕ_B^0 using the following expression:

$$\phi_B/\phi_B^0 = \exp(-\Delta^0 \rho x_B) = \exp(\rho x_B [G^{0}_{AA} + G^{0}_{BB} - 2G^{0}_{AB}]) \tag{10}$$

where Δ was defined in terms of the Kirkwood fluctuation integrals in Eq. (6) which are evaluated at the infinite dilution limit in this case.

The fugacity coefficient of a typical attractive solute decreases rapidly in a supercritical solvent as the solvent is compressed toward its CP. The dramatic effects on solubility of non-volatile solutes in supercritical solvents, then, follow directly from the changes that occur in the solution microstructure. The solubility effects form the basis of separations processes such as supercritical extraction and supercritical fluid chromatography. The equilibrium performance of the separation process may be predicted from theory based on understanding of the changing fluid microstructure. Applications to dilute binary supercritical solutions have been presented previously (32-34). The fundamental solubility equation from Kirkwood-Buff solution theory

$$kTd\rho_B = \rho_B G_{AB}\, dP + \sum_{i \neq A}^{c} [\rho_B \rho_i (G_{Bi} - G_{Ai}) + \delta_{Bi} \rho_B] d\mu_i \tag{11}$$

describes the behavior of solute B in solvent A in a c-component mixture. For a dilute solution of a pure, incompressible solid

$$kTd\rho_B/\rho_B = (G_{AB}^0 + v_B^s) dP \tag{12}$$

where v_B^s is the constant molecular volume of the solid. From Eq. (12) it is seen how the equilibrium solute concentration increases with the solvent-solute fluctuation integral, G_{AB}, for typical attractive solutions. For a dilute, repulsive solution, however, the sign of G_{AB} is *negative* so $d\rho_B/dP$ is negative, and the equilibrium solute concentration may be expected to exhibit a dramatic decrease as the pressure is raised toward the critical pressure. Also, for dilute repulsive solutions, solute partial molar volume is predicted to become large and *positive* near the critical point. The experimental results of Biggerstaff and Wood (15,16) support these predictions. The fugacity or chemical potential of a

dilute, repulsive solute is likewise predicted to increase dramatically as the pressure increases toward the critical pressure; thus, one might expect the solute to experience an increasing tendency to leave solution under such a compression.

The effects of a second solute and the effects of an added co-solvent on the solubility of B are expressed through Eq. (11) in terms of the Kirkwood fluctuation integrals which are directly related to the solution microstructure. Quantitative theoretical examination of these interactions in ternary supercritical solutions is to be presented in a forthcoming paper (35).

ACKNOWLEDGMENT

This work was supported in part by the Division of Chemical Sciences of the U. S. Department of Energy under contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc. and subcontract with the University of Oklahoma. The authors acknowledge programming and computations by D. M. Pfund.

REFERENCES

1. C. A. Eckert, D. H. Ziger, K. P. Johnston, and T. K. Ellison, "The Use of Partial Molar Volume Data to Evaluate Equations of State for Supercritical Fluid Mixtures," *Fl. Ph. Equilib.*, **14**, 167 (1983).

2. C. A. Eckert, D. H. Ziger, K. P. Johnston, and S. Kim, "Solute Partial Molar Volumes in Supercritical Fluids," *J. Phys. Chem.*, **90**, 2798 (1986).

3. S. Kim and K. P. Johnston, "Molecular Interactions in Dilute Supercritical Fluid Solutions," *I&EC Res.*, **26**, 1206 (1987).

4. C. R. Yonker, S. L. Frye, D. R. Kalkwarf, and R. D. Smith, "Characterization of Supercritical Fluid Solvents Using Solvatochromic Shifts," *J. Phys. Chem.*, **90**, 3022-3026 (1986).

5. S. Kim and K. P. Johnston, "Clustering in Supercritical Fluid Mixtures," *AIChE J.*, **33**, 1603-1611 (1987).

6. G. M. Schneider, J. Ellert, U. Haarhaus, I. F. Holscher, G. Katzenski-Ohling, A. Koppner, J. Kulka, D. Nickel, J. Rubesamen, and A. Wilsch, "Thermodynamic, Spectroscopic and Phase Equilibrium Investigations on Polar Fluid Mixtures at High Pressures," *Pure & Appl. Chem.*, **59**, 1115-1126 (1987).

7. C. R. Yonker and R. D. Smith, "Solvatochromic Behavior of Binary Supercritical Fluids: The Carbon Dioxide/2-Propanol System," *J. Phys. Chem.*, **92**, 2374-2378 (1988).

8. O. Kajimoto M. Futakami, T. Kobayashi, and K. Yamasaki, "Charge-Transfer-State Formation in Supercritical Fluid: (N,N-Dimetlylamino)benzonitrile in CF_3H," *J. Phys. Chem.*, **92**, 1347-1352 (1988).

9. K. P. Johnston, S. Kim, and J. Combs, "Spectroscopic Determination of Solvent Strength and Structure in Supercritical Fluid Mixtures, A Review," in *Supercritical Fluid Science and Technology*, K. P. Johnston and M. L. Penninger, Eds., ACS Symp. Ser. 406, Ch. 5, p. 52 (1989).

10. J. F. Brennecke and C. A. Eckert, "Molecular Interactions from Fluorescence Spectroscopy," *Proc. Int. Symp. on Supercritical Fluids*, M. Perrut, Ed., 263, Nice, France (1988).

11. J. F. Brennecke and C. A. Eckert, "Fluorescence Spectroscopy Studies of Intermolecular Interactions in Supercritical Fluids," in *Supercritical Fluid Science and Technology*, K. P. Johnston and J. M. L. Penninger, Eds., ACS Symp. Ser. No. 406, Ch. 2, p.14 (1989).

12. N. A. Collins, P. G. Debenedetti, and SD. Sundaresan, "Disproportionation of Toluene over ZSM-5 under Near-Critical Conditions," *AIChE J.*, **34**, 1121 (1988).

13. J. C. Wheeler, "Behavior of a Solute Near the Critical Point of an Almost Pure Solvent," *Ber. Bunsenges. Phys. Chem.*, **76**, 308 (1972).

14. P. G. Debenedetti and R. S. Mohamed, "Attractive, Weakly Attractive, and Repulsive Near-Critical Systems," *J. Chem. Phys.*, **90**, 4528 (1989).

15. D. R. Biggerstaff and R. H. Wood, "Apparent Molar Volumes of Aqueous Argon, Ethylene, and Xenon from 300 to 716 K," *J. Phys. Chem.*, **92**, 1988 (1988).

16. D. R. Biggerstaff and R. H. Wood, "Apparent Molar Heat Capacities of Aqueous Argon, Ethylene, and Xenon at Temperatures up to 720 K and Pressures to 33 MPa," *J. Phys. Chem.*, **92**, 1994 (1988).

17. P. G. Debenedetti, "Clustering in Dilute, Binary Supercritical Mixtures: A Fluctuation Analysis," *Chem. Eng. Sci.*, **42**, 2203 (1987).

18. J. G. Kirkwood and F. P. Buff, "The Statistical Mechanical Theory of Solutions. I.," *J. Chem. Phys.*, **19**, 774 (1951).

19. A. Munster, "Critical Fluctuations," in *Fluctuation Phenomena in Solids*, R. E. Burgess, Ed., Academic Press, 179 (1965).

20. J. S. Hoye and G. Stell, "Toward a Liquid State Theory with Accurate Critical Region Behavior," *Int. J. Thermophys.*, **6**, 561, (1985).

21. D. B. McGuigan and P. A. Monson, "Vapor-Liquid Critical Lines Predicted by Distribution Function Theories," *Mol. Phys.*, **62**, 3 (1987).

22. H. D. Cochran, L. L. Lee, and D. M. Pfund, "Study of Fluctuations in Supercritical Solutions by an Integral Equation Method," *Proc. Int. Symp. on Supercritical Fluids*, M. Perrut, Ed., Nice, France, 245 (1988).

23. H. D. Cochran and L. L. Lee, "Solvation Structure in Supercritical Fluid Mixtures based on Molecular Distribution Functions," in *Supercritical Fluid Science and Technology*, K. P. Johnston and J. M. L. Penninger, Eds., ACS Symp. Ser. 406, Ch. 3, p. 27 (1989).

24. H. D. Cochran, L. L. Lee, and D. M. Pfund, "Structure and Properties of Supercritical Fluid Mixtures from Kirkwood-Buff Fluctuation Theory and Integral Equation Methods," submitted to *Fluctuation Theory of Mixtures*, E. Matteoli, Ed., Adv. in Thermo. Ser., Taylor and Francis (1989).

25. L. L. Lee, P. G. Debenedetti, and H. D.Cochran, "Fluctuation Theory of Supercritical Solutions," *Supercritical Fluid Technology*, T. J. Bruno and J. F. Ely, eds., CRC Press,

submitted (1989).

26. R.-S. Wu, L. L. Lee, and H. D. Cochran, "The Structure of Dilute Supercritical Solutions: Clustering of Solvent and Solute Molecules and the Thermodynamic Effects," *I&EC Res.*, submitted (1989).

27. L. L. Lee , *Molecular Thermodynamics for Nonideal Fluids*, Butterworths, Boston (1988).

28. D. B. McGuigan and P. A. Monson, "Analysis of Infinite Dilution Partial Molar Volumes Using a Distribution Function Theory," *Fl. Ph. Equilib.*, in press (1989).

29. I. B. Petsche and P. G. Debebedetti, "Solute-Solvent Interactions in Infinitely Dilute Supercritical Mixtures: A Molecular Dynamics Investigation," *J. Chem. Phys.*, **91**, 7075 (1989).

30. H. D. Cochran and L. L. Lee, "General Behavior of Dilute Binary Solutions," *AIChE J.*, **33**, 1391 (1987) and *ibid.*, **34**, 170 (1988).

31. P. G. Debenedetti and S. K. Kumar, "Infinite Dilution Fugacity Coefficients and the General Behavior of Dilute Binary Systems," *AIChE J.*, **32**, 1253 (1986).

32. H. D. Cochran, L. L. Lee, and D. M. Pfund, "Application of the Kirkwood-Buff Theory of Solutions to Dilute Supercritical Mixtures," *Fl. Ph. Equilib.*, **34**, 219 (1987).

33. D. M. Pfund, L. L. Lee, and H. D. Cochran, "Application of the Kirkwood-Buff Theory of Solutions to Dilute Supercritical Mixtures. II. The Excluded Volume and Local Composition Models," *Fl. Ph. Equilib.*, **39**, 161 (1988).

34. H. D. Cochran, D. M. Pfund, and L. L. Lee, "Theoretical Models of Thermodynamic Properties of Supercritical Solutions," *Sep. Sci. & Tech.*, **23**, 2031 (1988).

35. H. D. Cochran, E. Johnson, and L. L. Lee, "Molecular Theory of Ternary Supercritical Solutions," *J. Supercritical Fluids*, to be published.