Fluctuation Theory of Hydrogen Bonding in Near-Critical Fluids

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Recent experiments indicate that the number of hydrogen bonds in solutions increases in the critical region of the solvent. This effect can be explained by the density fluctuations near the critical point. A theory of this unusual effect is developed. The theoretical predictions are compared with the experimental data on hydrogen bonding between perfluoro-tert-butanol and dimethyl ether in supercritical sulfur hexafluoride. The theory requires no adjustable parameters and is in excellent agreement with the experimental data. Possible applications of this effect for hydrogen-bonding solutions and polymer mixtures are discussed.

Introduction

Hydrogen bonding is an important interaction in fundamental and applied science. Actually it is as important as the carbon–carbon bond (Pimentel and McClellan, 1960). It is the most common specific interaction in the thermodynamics of solutions (Prausnitz et al., 1986). The formation of hydrogen bonds in fluids modifies their physical and chemical properties in many ways. In particular, it substantially changes freezing and boiling points, solubilities of various substances, dielectric properties and electrical conductivity, vapor pressure, and density.

In the chemical industry hydrogen bonding plays a vital role in various areas: physical networks and gels, nonionic surfactants, ordering and association in microemulsions, microphase separation and interfacial phenomena in block copolymers, properties of aqueous multiphase systems, selective extraction of fermentation products, folding and association of proteins, behavior of water-soluble polymers, polymer compatibilization, and thermodynamic properties of gasohol (Vinogradov and Linnell, 1971; Walter et al., 1985; Burchard and Ross-Murphy, 1990; Reichardt, 1984; Panayiotou and Sanchez, 1991). Also, in supercritical fluid technology, hydrogen bonding plays an important role in separation and chemical processing of polar compounds (Dobbs et al., 1987; Lemert and Johnston, 1991), hydrothermal reactions (Antal et al., 1987), and supercritical water oxidation processes (Thornton and Savage, 1990; Yang and Eckert, 1988; Webley and Tester, 1991). Therefore the study of the degree of hydrogen bonding in supercritical fluids interested a number of researchers (Nickel and Schneider, 1989; Fulton et al., 1991; Ochel and Schneider, 1994a,b; Maiwald and Schneider, 1995).

A century of experimental study of hydrogen bonding clearly indicates that the solvent is not merely a passive agent. Rather, it can have a pronounced influence on the formation of the hydrogen-bonded complex. Recently, experiments of Gupta et al. (1993), based on Fourier transform infrared (FTIR) spectroscopy, have indicated that hydrogen bonding is influenced by a relatively inert supercritical solvent. A pronounced solvent effect on the hydrogen bonding of methanol and triethylamine was observed throughout the gas, supercritical, and liquid states of SF_6. It was found that the hydrogen bonding increased as the solvent density decreased. The hydrogen bonding lattice fluid model (LFHB), originally introduced by Veytsman (1990), was extended to treat this density dependence, and the calculations were in good agreement with the experiment (see Gupta et al., 1992; Gupta et al., 1993).

Another effect was observed near the critical point of the mixture. It was found by Gupta et al. (1993) that the number

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of hydrogen bonds near the critical point is greater than predicted by the LFHB theory. It was supposed that contacts between the hydrogen bonding species are enhanced due to solute–solute clustering. This near-critical enhancement is not described by the mean-field LFHB model. These results were confirmed in a later study by Kazarian et al. (1993). In their work FTIR spectroscopy was used to study the effects of solvent density on the hydrogen-bonding equilibrium between perfluoro-tertiary butanol (PFTB), $(CF_3)_3COH$, and dimethyl ether (DME), $(CH_3)_2O$ in SF_6 solvent. Near the critical region, enhanced hydrogen bonding was observed. This anomalous behavior was attributed to the solute–solute clustering that has also been observed in many other studies: in an electron paramagnetic resonance (EPR) spectroscopic study of cholesterol (Randolph et al., 1988), steady-state fluorescence studies of pyrene excimer formation (Brennecke and Eckert, 1989), photodimerization of cyclohexanone (Combes et al., 1992), and the photochemical hydrogen abstraction reaction between benzophenone and isopropanol (Chateauneuf et al., 1992). Recently, it was found that the clustering effect in the hydrogen bonding in polymer melts is rather significant (Veytsman and Painter, 1993; Painter et al., 1994). So it is not surprising that clustering influences hydrogen bonding in the near-critical mixtures, where density fluctuations are high. Nevertheless, up until now there was no theory of the hydrogen-bonding enhancement in near-critical solutions. The present article is intended to close this gap.

In this work we develop a model based on density fluctuation theory to describe the enhanced hydrogen-bonding phenomenon in the near-critical region. This theory predicts an enhancement of hydrogen bonding near the critical point in good agreement with the experimental data.

Qualitative Picture

Let us discuss a dilute solution of two hydrogen-bonding species, 1 and 2. The prototype for such system is a solution of PFTB and DME in SF_6, studied by Kazarian et al. (1993). PFTB has one proton donor site, and DME has one proton acceptor site, hence a 1–1 hydrogen bond is formed between these two molecules, if they are close to each other. The extent of hydrogen bonding depends on the concentration of the components as well as the temperature and solvent density. Far from the critical point the fluctuations are small, and the concentration of solute molecules is approximately constant throughout the system. However, near the critical point, the fluctuations increase. Some regions have local density greater than the average, while other regions have local density lower than the average. Since chemical potentials of the solute molecules—and therefore their concentrations—depend on the density of the solution, these regions become enriched or depleted in the solute. If the regions depleted in the solute 1 are enriched in the solute 2, fluctuations tend to segregate hydrogen-bonding molecules, and the number of hydrogen bonds decrease. On the other hand, if the regions enriched in the solute 1 are *simultaneously* enriched in the solvent 2, the contacts between the hydrogen-bonding species are facilitated, and the fluctuations increase the number of hydrogen bonds. We call this effect *fluctuation correction*. The calculation of the fluctuation correction is the aim of this article.

Theory of the Fluctuation Correction to the Hydrogen Bonding

In the absence of fluctuations, the following stoichiometry equation (Veytsman, 1990; Coleman et al., 1991; Sanchez and Panayiotou, 1994) holds:

$$m=(n_1-m)(n_2-m)K, \tag{1}$$

where n_1 and n_2 are the concentrations of the solvents (in molecules per unit volume), K is the hydrogen-bonding constant, and m is the concentration of H-bonds (i.e., the number of hydrogen bonds in the unit volume). However, near the critical point the fluctuations are high, so n_1, n_2, and m are different at different places. Therefore we should rewrite Eq. 1 to include only the local values of the thermodynamic parameters.

Let us divide the system into a number of small "boxes" having volume V_0 each. This volume should be small enough to allow us to neglect the differences in the thermodynamic parameters in the different parts of the box. On the other hand, it should be large enough to allow us to use macroscopic thermodynamics for the processes in the box. We will discuss the choice of the volume V_0 in more detail below. Let r be the coordinate of the center of the box. If we understand by $n_1(r)$, $n_2(r)$, $m(r)$ the values measured in the box, then we can write the *local* stoichiometry equation:

$$m(r)=[n_1(r)-m(r)][n_2(r)-m(r)]K. \tag{2}$$

In the experiments we measure the average value $\overline{m}=\langle m(r)\rangle$, where brackets $\langle\ldots\rangle$ mean the averaging over a large sample volume V containing many "boxes." To average Eq. 2 we will introduce the average values $\overline{m}$, $\overline{n}_1$, $\overline{n}_2$, and the local fluctuations $\delta m(r)$, $\delta n_1(r)$, and $\delta n_2(r)$:

$$\begin{aligned} m(r)&=\overline{m}+\delta m(r)\\ n_i(r)&=\overline{n}_i+\delta n_i(r), \qquad i=1,2 \end{aligned} \tag{3}$$

with zero average values of deviations:

$$\langle\delta m\rangle=\langle\delta n_1\rangle=\langle\delta n_2\rangle=0. \tag{4}$$

If the system is not too close to the critical point, we can expand Eq. 2 around the nonfluctuating values $\overline{n}_1$ and $\overline{n}_2$:

$$\begin{aligned} m(r)=m_0&+\frac{\partial m_0}{\partial\overline{n}_1}\delta n_1(r)+\frac{\partial m_0}{\partial\overline{n}_2}\delta n_2(r)+\frac{1}{2}\frac{\partial^2 m_0}{\partial\overline{n}_1^2}\delta n_1^2(r)\\ &+\frac{\partial^2 m_0}{\partial\overline{n}_1\partial\overline{n}_2}\delta n_1(r)\delta n_2(r)+\frac{1}{2}\frac{\partial^2 m_0}{\partial\overline{n}_2^2}\delta n_2^2(r)+\cdots, \end{aligned} \tag{5}$$

where m_0 is the solution of the stoichiometry equation in the absence of fluctuations:

$$m_0=(\overline{n}_1-m_0)(\overline{n}_2-m_0)K. \tag{6}$$

Averaging Eq. 5 and using Eq. 4 we obtain

$$\bar{m} = m_0 + \frac{1}{2}\frac{\partial^2 m_0}{\partial \bar{n}_1^2}\langle \delta n_1^2\rangle + \frac{\partial^2 m_0}{\partial \bar{n}_1 \partial \bar{n}_2}\langle \delta n_1 \delta n_2\rangle + \frac{1}{2}\frac{\partial^2 m_0}{\partial \bar{n}_2^2}\langle \delta n_2^2\rangle + \cdots. \quad (7)$$

The derivatives of m_0 can be obtained from Eq. 6:

$$\frac{\partial m_0}{\partial \bar{n}_i} = \frac{m_0(\bar{n}_1 - m_0)(\bar{n}_2 - m_0)}{(\bar{n}_i - m_0)(\bar{n}_1\bar{n}_2 - m_0^2)}, \qquad i = 1,2 \quad (8)$$

and

$$\frac{\partial^2 m_0}{\partial \bar{n}_i^2} = -\frac{2\bar{n}_1\bar{n}_2 m_0^2(\bar{n}_1 - m_0)(\bar{n}_2 - m_0)}{(\bar{n}_1\bar{n}_2 - m_0^2)^3 \bar{n}_i}$$

$$\frac{\partial^2 m_0}{\partial \bar{n}_1 \partial \bar{n}_2} = \frac{m_0(\bar{n}_1 - m_0)(\bar{n}_2 - m_0)(\bar{n}_1\bar{n}_2 + m_0^2)}{(\bar{n}_1\bar{n}_2 - m_0^2)^3} \quad (9)$$

To calculate the correlation functions of δn_1 and δn_2 let us note that the main fluctuating parameter in the system is the total density $\rho(\boldsymbol{r})$. Using the method of Jacobians (see, e.g., Landau and Lifshitz, 1980, 1981) we can write for n_1:

$$\delta n_1(\boldsymbol{r}) = A_1 \delta\rho(\boldsymbol{r}), \quad (10)$$

with

$$A_1 = \left(\frac{\partial n_1}{\partial \rho}\right)_{\mu_1,\mu_2} = \frac{\partial(n_1,\mu_1,\mu_2)}{\partial(\rho,\mu_1,\mu_2)} = \frac{\Delta_1}{\Delta_0}, \quad (11)$$

where μ_i are the corresponding chemical potentials, defined as the derivatives of the free energy F with respect to the numbers of solute molecules:

$$\mu_1 = \left(\frac{\partial F}{\partial n_1}\right)_{n_2,\rho}, \qquad \mu_2 = \left(\frac{\partial F}{\partial n_2}\right)_{n_1,\rho}, \quad (12)$$

and Δ_1 and Δ_0 are the Jacobi determinants:

$$\Delta_1 = \frac{\partial(n_1,\mu_1,\mu_2)}{\partial(n_1,n_2,\rho)} = \begin{vmatrix} \left(\frac{\partial \mu_1}{\partial n_2}\right)_{n_1,\rho} & \left(\frac{\partial \mu_1}{\partial \rho}\right)_{n_1,n_2} \\ \left(\frac{\partial \mu_2}{\partial n_2}\right)_{n_1,\rho} & \left(\frac{\partial \mu_2}{\partial \rho}\right)_{n_1,n_2} \end{vmatrix}$$

$$\Delta_0 = \frac{\partial(\rho,\mu_1,\mu_2)}{\partial(n_1,n_2,\rho)} = \begin{vmatrix} \left(\frac{\partial \mu_1}{\partial n_1}\right)_{n_2,\rho} & \left(\frac{\partial \mu_1}{\partial n_2}\right)_{n_1,\rho} \\ \left(\frac{\partial \mu_2}{\partial n_1}\right)_{n_2,\rho} & \left(\frac{\partial \mu_2}{\partial n_2}\right)_{n_1,\rho} \end{vmatrix}. \quad (13)$$

Analogously we can write for $\delta n_2(\boldsymbol{r})$:

$$\delta n_2(\boldsymbol{r}) = A_2 \delta\rho(\boldsymbol{r}), \quad (14)$$

where A_2 is determined by the equations analogous to Eqs. 11 and 13 after substitution $1 \leftrightarrow 2$.

Combining these expressions, we see that the number of hydrogen bonds is

$$\bar{m} = m_0 + \Delta m \quad (15)$$

where the fluctuation correction is determined by the following equation:

$$\Delta m = \langle \delta\rho^2(\boldsymbol{r})\rangle \frac{(\bar{n}_1 - m_0)(\bar{n}_2 - m_0)m_0}{(\bar{n}_1\bar{n}_2 - m_0^2)^3}[A_1A_2(\bar{n}_1\bar{n}_2 + m_0^2) - m_0(\bar{n}_1A_2^2 + \bar{n}_2A_1^2)]. \quad (16)$$

Since at the critical point $\langle \delta\rho^2\rangle \to \infty$, the fluctuation correction diverges near the critical point, as it should be expected.

Equation 16 contains two parameters, A_1 and A_2. Their physical meaning is simple. They determine how the solute reacts to the change in the solvent's density. If $A_i > 0$, the regions of higher solvent density are enriched in the corresponding solute; if $A_i < 0$, they are depleted. If the solution is very diluted, $\partial\mu_1/\partial n_2 = \partial\mu_2/\partial n_1 = 0$, and we have

$$A_i = \frac{\partial\mu_i/\partial\rho}{\partial\mu_i/\partial n_i}. \quad (17)$$

Let us discuss the sign of the correction. It is easy to see that all terms in Eq. 16 but the one in square brackets is always positive. Therefore the sign of the correction is determined by the sign of the term $[A_1A_2(\bar{n}_1\bar{n}_2 + m_0^2) - m_0(\bar{n}_1A_2^2 + \bar{n}_2A_1^2)]$. We can determine it *a priori* for several important limiting cases.

First suppose that the solvent reacts with both solutes exactly in the same way. This means that $A_1 = A_2$. It is easy to see from Eq. 16 that in this case Δm is *always* nonnegative, and fluctuations are favorable for hydrogen bonding. Qualitatively, this is quite understandable: If fluctuations in the solvent density have the same effect on both solutes, the clustering is favorable for hydrogen bonding. In the case of $m_0 \ll \min(\bar{n}_1, \bar{n}_2)$, the condition for Δm to be positive is even weaker: It is enough for A_1 and A_2 to have the same signs.

Suppose now that A_1 and A_2 have different signs. Then Δm is always negative. Once again, this is understandable: If the regions of higher solvent density are enriched in one solute and depleted in another, fluctuations cause segregation of hydrogen-bonding species, thus decreasing the number of hydrogen bonds.

Up to now our considerations were quite general. To calculate the righthand side of Eq. 16 we must, however, make some assumptions about the system. We will do this for the case of dilute mixtures, because for this case we have experimental data available. The average fluctuation of the density in the "box" of the volume V_0 is determined by the compressibility of the system (see, e.g., Landau and Lifshitz, 1980, 1981):

$$\langle \delta\rho^2\rangle = \frac{kT\rho}{V_0}\left(\frac{\partial\rho}{\partial p}\right)_T, \quad (18)$$

where k is Boltzmann's constant, T is the temperature, and p is the pressure. This equation includes the volume V_0 of the "box." It cannot be determined in a purely macroscopic way. We must use the molecular picture of the processes in the system to obtain this parameter. This problem is very close to the problem of the cutoff length in the renormalization group theory of the critical point (see Patashinskii and Pokrovskii, 1979). In both cases the macroscopic theory gives us all critical singularities up to some microscopic "molecular length" that must be put in the theory by hand.

Let us consider an elementary process of the formation of the hydrogen bond between the molecules A and B:

$$A + B \rightleftharpoons A \cdots B. \tag{19}$$

The characteristic volume associated with this process is the volume $\pi a^3/6$ of a sphere with the diameter a, equal to the average distance between the free molecules A and B in the solution. Only the fluctuations in this volume directly affect the rate of the "reaction," Eq. 19. Therefore the volume of the "box" V_0 should be close to the characteristic volume $\pi a^3/6$. In dilute solutions the distance a can be estimated as $a \sim (\bar{n}_1 \bar{n}_2)^{-1/6}$, and therefore

$$V_0 \approx \frac{\pi}{6} \frac{1}{\sqrt{\bar{n}_1 \bar{n}_2}}. \tag{20}$$

Actually the factor $\pi/6$ in this equation seems to be extraneous. Obviously our simple considerations are not exact enough to give the numerical factor in Eq. 20. Perhaps it would be more prudent to substitute for it some dimensionless parameter c of the order of unity. However, it turns out (see the next section) that the factor $\pi/6$ reproduces the experimental data remarkably well. We discuss this below.

Now let us calculate the factors A_i. We will use the fact that the solution is dilute. For ideal solutions the chemical potential of solute is (see Landau and Lifshitz, 1980, 1981)

$$\mu_i^{\text{ideal}} = kT \ln n_i + \psi_i(\rho), \qquad i = 1,2, \tag{21}$$

where the functions ψ_i do not depend on n_i. For dilute solutions we can neglect all interactions between the solute molecules *but* hydrogen bonding. Then we have

$$\mu_i = \mu_i^{\text{ideal}} + \frac{\partial F_{HB}}{\partial n_i}, \qquad i = 1,2, \tag{22}$$

where F_{HB} is the contribution of hydrogen bonds, equal to (Veytsman, 1990)

$$F_{HB} = kT\left[m + n_1 \ln\left(1 - \frac{m}{n_1}\right) + n_2 \ln\left(1 - \frac{m}{n_2}\right)\right]. \tag{23}$$

Differentiating Eq. 23 with respect to n_i, and using Eq. 2, we obtain

$$\mu_i = kT \ln(n_i - m) + \psi_i(\rho). \tag{24}$$

When differentiating chemical potentials with respect to ρ we must keep in mind that both terms in Eq. 22 depend on the density: the last term directly, and the first one through the equilibrium constant K. The correlation (Kazarian et al., 1993) gives

$$\frac{\partial K}{\partial \rho} = -\frac{f'}{\rho^* kT} K, \tag{25}$$

where ρ^* is a lattice fluid parameter (Sanchez and Panayiotou, 1994) and f' is a constant parameter (in the paper by Kazarian et al. the parameter f' was called F'_{11}). After some algebra, we obtain

$$\begin{aligned} A_1 &= -\frac{f' m_0}{\rho^* kT} - \frac{m_0}{kT}\frac{\partial \psi_2}{\partial \rho} - \frac{\bar{n}_1}{kT}\frac{\partial \psi_1}{\partial \rho} \\ A_2 &= -\frac{f' m_0}{\rho^* kT} - \frac{m_0}{kT}\frac{\partial \psi_1}{\partial \rho} - \frac{\bar{n}_2}{kT}\frac{\partial \psi_2}{\partial \rho}, \end{aligned} \tag{26}$$

and Eq. 16 can be rewritten as

$$\Delta m = \frac{\rho kT}{(\rho^*)^2 V_0}\left(\frac{\partial \rho}{\partial p}\right)_T \frac{(\bar{n}_1 - m_0)(\bar{n}_2 - m_0) m_0}{(\bar{n}_1 \bar{n}_2 - m_0^2)} X_1 X_2, \tag{27}$$

where X_i are dimensionless parameters

$$X_i = \frac{\rho^*}{kT}\frac{\partial \psi_i}{\partial \rho} + \frac{f' m_0 (\bar{n}_1 - m_0)(\bar{n}_2 - m_0)}{kT(\bar{n}_i - m_0)(\bar{n}_1 \bar{n}_2 - m_0^2)}, \qquad i = 1,2. \tag{28}$$

The derivatives $\partial \psi_i / \partial \rho$ are related to the heats of mixing of the solute with the solvent q_i. Indeed, the latter is proportional to $\exp(-\psi_i/kT)$ (see, e.g., Landau and Lifschitz, 1980, 1981). Taking the log of the equation $q_i =$ const $\exp(-\psi_i/kT)$ and differentiating, we obtain

$$\frac{\partial \psi_i}{\partial \rho} = -\frac{kT}{q_i}\frac{\partial q_i}{\partial \rho}. \tag{29}$$

Comparison with the Experimental Data

In this section we compare Eq. 27 with the experimental data of Kazarian et al. (1993) on the hydrogen bonding of PFTB and DME in supercritical SF_6. As can be seen from the experimental data (Figures 1 and 2), the observed hydrogen bonding is enhanced near the critical point of sulfur hexafluoride (temperature $T_c = 45.5$°C, density $\rho_c = 5.03$ mol/L).

In the subsequent numerical calculations the LFHB parameters are taken from the paper by Kazarian et al. (1993). The density and isothermic compressibility of pure sulfur hexafluoride are obtained from the correlation by Biswas et al. (1984) (see also correction by Biswas et al., 1988).

As follows from Eq. 29, the determination of the derivatives $\partial \psi_i / \partial \rho$ can be based on the experimental data on the heat of mixing. Unfortunately we don't have reliable data on the density dependence of q_i. Therefore we must use some model for the functions ψ_i. The most commonly used model is the lattice fluid equation of state (Sanchez and Panayioutou,

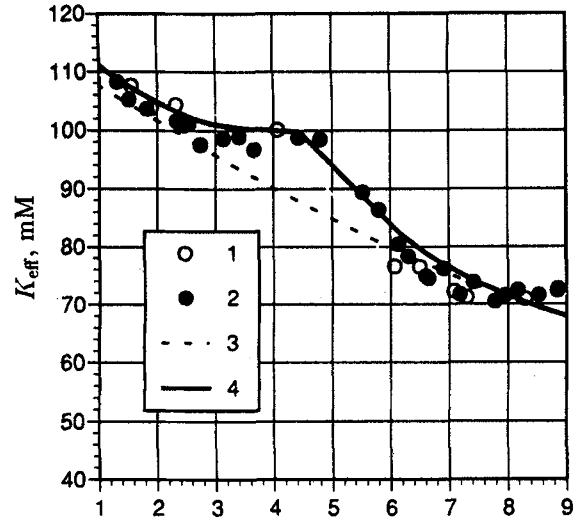

Figure 1. Effective constant $K_{\rm eff}$ of hydrogen bond formation for PFTB and DME in supercritical SF_6 near the critical point of the solvent (T_c = 45.5°C, $\rho_c = 5.03$ mol/L).

Experimental data are from Kazarian et al. (1993). $T = 50$°C. 1—Experimental data for 1.5-mM PFTB and 25-mM DME; 2—experimental data for 2-mM PFTB and 15-mM DME; 3—mean field theory; 4—fluctuation theory.

1994). For dilute solutions it gives (up to inessential additive constants):

$$\psi_i = kTr_i\left[\frac{P\rho^* T_i^*}{P_i^*\rho T} - \frac{\rho T_i^*}{\rho^* T} + \ln\left(1-\frac{\rho}{\rho^*}\right)\left(\frac{\rho^*}{\rho}-1\right)\right], \quad (30)$$

where r_i, ρ^*, ρ_i^*, T^*, T_i^*, P^*, P_i^* are the lattice parameters (see Sanchez and Panayiotou, 1994). The subscript i refers to the solute ($i = 1,2$), and the parameters without subscript refer to the solvent.

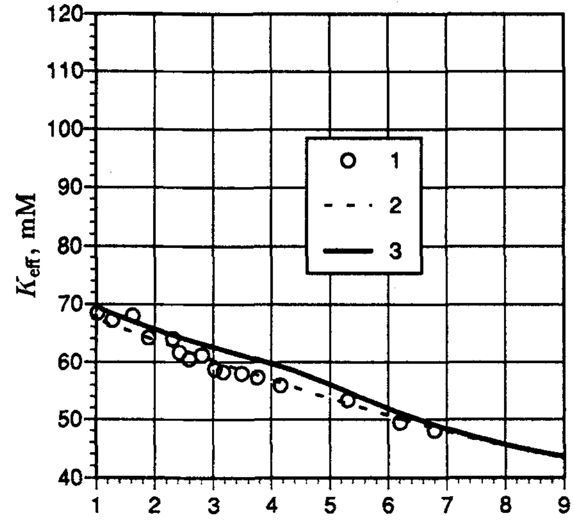

Figure 2. Same as Figure 1, but relatively far from the critical point of the solvent, $T = 60$°C.

1—Experimental data for 1.2-mM PFTB and 30-mM DME; 2—mean field theory; 3—fluctuation theory.

The results of calculations are presented on Figures 1 and 2. Following Kazarian et al. (1993), we plot the effective hydrogen-bonding constant K, defined as

$$K_{\rm eff} = \frac{\overline{m}}{(\overline{n}_1 - \overline{m})(\overline{n}_2 - \overline{m})}, \quad (31)$$

as the function of the density. Figure 1 represents the predicted and measured values of $K_{\rm eff}$ for the temperature T = 50°C—relatively close to the critical temperature T_c = 45.5°C of SF_6. (Strictly speaking, the predictions for $K_{\rm eff}$ are different for the two sets of n_1 and n_2 represented on Figure 1. However, the difference is everywhere smaller than 1 mM, so we plotted only the theoretical curve for 2 mM PFTB and 16 mM DME.) The success of the theoretical predictions is surprising. It becomes even more remarkable if we note that our calculations of Δm *do not contain any adjustable parameters at all!*

Figure 2 shows the predicted and measured values of $K_{\rm eff}$ for the temperature T = 60°C—relatively far from the critical temperature T_c = 45.5°C of SF_6. The fluctuation correction at this temperature is quite small and is below the accuracy of the experiment.

Assumptions and Limitations

Let us discuss how general our results are.

The main assumption we made is that the fluctuation correction is small:

$$\Delta m \ll m_0. \quad (32)$$

It allowed us to use the expansion in Eq. 5. This assumption is valid for the existing experimental data, but is violated in the very close vicinity of the critical point. The situation in the close vicinity of the critical point requires sophisticated methods of averaging Eq. 2 that are beyond the scope of this article.

Once the condition in Eq. 32 is satisfied, our theory is quite general up to Eq. 16. Then we used the assumption that the mixture is dilute while calculating V_0 and A_i. At higher concentrations we need to know the details of the molecular interactions to make quantitative predictions for V_0 and A_i. It seems reasonable that the theory developed in this article will remain at least qualitatively correct even at higher concentrations.

It is interesting to see how good our prediction for V_0 is. The rigorous determination of the numerical factor in Eq. 20 is difficult and may be impossible for the general case. Our simple considerations suggest that this factor is close to $\pi/6$; it is possible that the real value is slightly different and is system dependent. The experimental data are reproduced more or less well if we vary this factor from 0.45 to 0.65.

We used the Sanchez–Lacombe equation of state to determine A_i. It should be noted that this equation is not especially good near the critical point in predicting the chemical potentials. The reason why Eq. 27 adequately reproduces the *shape* of the $K_{\rm eff}$ vs. ρ curve is that the main contribution in this equation is from the factor $(\partial \rho/\partial p)_T$. We used very accurate values of this factor for pure SF_6 (Biswas et al., 1984, 1988). This almost singular contribution suppresses uncertainties in all other factors.

Applications

The enhancement of the hydrogen bonding might be of interest for many industrial applications discussed in the Introduction. The present theory suggests two ways to increase this enhancement: getting close to the critical point and increasing the concentration of hydrogen-bonding specii. In both cases the ratio $\Delta m/m_0$ should increase. In the first case, it grows as the compressibility, that is, as $|T-T_c|^{-\gamma}$, where $\gamma = 1$ in the Landau region and $\gamma = 4/3$ in the scaling region (see Patashinskii and Pokrovskii, 1979). In the second case it grows as the inverse volume V_0^{-1}, that is, as $(\bar{n}_1\bar{n}_2)^{1/2}$.

Another interesting application of the effect being discussed is the study of the critical phenomena in opaque liquids. The convenient technique of light scattering on the density fluctuations does not work for such systems. One can add some hydrogen bonding specii to such solutions as probes and measure the degree of hydrogen bonding using FTIR spectroscopy. This application might be of special interest for polymers where the conventional methods of study of the critical phenomena often do not work. FTIR spectroscopy of the hydrogen bond turned out to be very useful for the study of first-order phase transitions in polymers (see Coleman et al., 1991). This theory suggests that it might also be useful for the study of critical points and the second-order transitions.

Conclusion

In this article we developed a theory of density fluctuations correction to the degree of hydrogen bonding in near critical solutions. This correction is significant in the vicinity of the critical point, but decreases away from it along with the density–density correlation function. The sign of the correction depends on the solvent–solute interactions. If the interaction energies are close, the correction is positive, and the number of hydrogen bonds increases in the vicinity of the critical point.

The present theory is in good agreement with the experimental data and can be used for predicting the degree of hydrogen bonding in near-critical solutions.

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Notation

A_i = coefficients in the Eq. 11
γ = critical index of compressibility
$\delta\rho$ = local fluctuation of the density

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