Dynamic Light-Scattering Study of Tetrahydrofuran and Water Solutions

C. M. Sorensen

Department of Physics, Kansas State University, Manhattan, Kansas 66506 (Received: July 17, 1987; In Final Form: October 23, 1987)

Dynamic light-scattering experiments on solutions of tetrahydrofuran (THF) and water at various temperatures are reported. These measurements indicate that the correlation length of concentration fluctuations in this mixture is determined by a liquid–liquid lower critical solution point near 71.85 °C and 22.5 mol % THF. This effect is clearly seen even far from the critical point at 25 °C. It is proposed that the molecular origin of these fluctuations is THF–water hydrogen bonding and that other anomalous properties of this system near room temperatures are the result of these critical phenomena fluctuations. Generalization of these results to other aqueous solutions is proposed.

I. Introduction

The properties of aqueous solutions of small nonpolar or mixed solutes have provided both stimulation and puzzlement for physical chemists for some time.[1] These systems display unusual and anomalous behavior in a variety of their thermodynamic and transport properties. The molecular origins of these unusual properties have long been sought and are often ascribed to hydrogen-bond interactions between the solute and water molecules, or self-association between the water molecules themselves, which seems to be stimulated by the hydrophobic group on the solute molecule. Despite considerable effort and enlightenment over the years, no coherent picture useful to describe in general the anomalous properties of these solutions has appeared.

In earlier work we have studied aqueous solutions of *tert*-butyl alcohol.[2-4] This system displays a fascinating variety of phenomena which suggest structures form in the solution. In particular, clathrate-like structures, self-associated water molecules forming cages with small voids,[5] have been proposed to explain some of the X-ray[6] and light-scattering[3,7] experimental results. We have taken the point of view that while such clathrate structures may well form in these solutions, the anomalous properties might better be explained in terms of liquid–liquid critical points that may or may not lie on the equilibrium phase diagram of the pure system.[3] We have seen that equilibrium critical points appear at both supercooled and high temperatures upon addition of the isomer *sec*-butyl alcohol,[4] and these critical points can be used to describe the unusual light and X-ray scattering properties. Thus, the relevant structures for the macroscopic properties of the solution may be the critical phenomena concentration fluctuations which, regardless of their molecular origins, appear in these solutions.

In this paper I report a light-scattering study for solution of tetrahydrofuran (THF) and water. Past studies of this system have implicated the importance of pseudoclathrate structures[8] and fluctuations[9] in determining the properties of this system. In particular, sound absorbtion measurements by Atkinson, Rajagopalan, and Atkinson[9] have indicated that concentration fluctuations best explain their data. The work presented here will show that these fluctuations do indeed exist and are the result of a critical point at the lower extreme of a liquid–liquid miscibility gap in the superheated (relative to boiling) solution.

In the next section I will describe the photon correlation spectroscopy (PCS) light-scattering experiment used to determine the relaxation time of the concentration fluctuations. Section III analyzes the results by demonstrating that the correlation length of the fluctuations follows the standard power-law divergence along the critical concentration as the critical temperature is approached. Despite the fact that this critical point is at ~71.85 °C and in the superheated regime, its effects are felt at 25 °C. I then present a somewhat novel analysis using the pseudospinodal assumption to show that other solution concentrations are affected by this critical point. Section IV concludes this work with suggestions about critical points and their effects on aqueous solutions in general.

II. Experimental Method

Samples were prepared volumetrically from high-purity tetrahydrofuran (Aldrich Gold Label) and distilled and then deionized water (H_2O).

Roughly 3 mL of solution was placed in a 1-cm² spectrophotometer cuvette. An O-ring seal cap was specially made for this cuvette to stop leakage of the sample which had occurred at high temperature in early experiments. The cuvette was mounted in a solid brass cylinder which fitted into a two-stage temperature-controlled cell. Thermistors were used to detect the temperature, and proportional feedback from sensitive resistance bridges allowed for millikelvin control.

The light-scattering apparatus for the photon correlation spectroscopy[10] experiment consisted of an argon ion laser which operated between ~10 and 300 mW at λ = 5145 Å. The vertically polarized incident beam was focused through a 30-cm lens into the sample. Scattered light was collected by another lens and imaged onto a 300-μm pinhole. The scattering angle was 30.8° in the liquid. The light diffracted by the pinhole fell on the cathode of an ITT FW130 photomultiplier. The resultant photopulses were amplified, discriminated and passed to a commerical correlator which calculated the scattered-light intensity autocorrelation function. Due to the large distances in temperature from the critical point, multiple scattering was never a problem.

Analysis of the correlation function used the equation

$$\langle I(t)\, I(0)\rangle = B + Ae^{-\mu_1 t + (1/2)\mu_2 t^2} \tag{1}$$

In eq 1 B and A are experimentally determined background and signal amplitudes, and μ_1 and μ_2 are the first two cumulants. Fits to eq 1 were obtained by measuring B at large t and then performing a least-squares fit with A, μ_1, and μ_2 as variables. Random errors in μ_1 were 2% or better.

Light scattering was performed at temperatures from 25 to (usually) 65 °C. According to Matous et al.,[11] the equilibrium

(1) Franks, F.; Reid, D. S. In *Water, A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1973; Vol. 2.
(2) Sorensen, C. M. *J. Chem. Phys.* **1983**, *79*, 1455.
(3) Euliss, G. W.; Sorensen, C. M. *J. Chem. Phys.* **1984**, *80*, 4767.
(4) Sorensen, C. M. submitted for publication in *J. Chem. Phys.*
(5) Davidson, D. W. In *Water, A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1973; Vol. 2.
(6) Bale, H. D.; Shepler, R. E.; Sorgen, D. K. *Phys. Chem. Liq.* **1968**, *1*, 181.
(7) Iwasaki, K.; Fujiyama, T. *J. Phys. Chem.* **1977**, *81*, 1908; **1979**, *83*, 463.
(8) Gough, S. R. *J. Solution Chem.* **1979**, *8*, 371.
(9) Atkinson, G.; Rajagopalan, S.; Atkinson, B. L. *J. Phys. Chem.* **1981**, *85*, 733.

(10) For a review see: Berne, B. J.; Pecora, R. *J. Dynamic Light Scattering*; Wiley: New York, 1976. Chu, B. *Laser Light Scattering*; Academic: New York, 1974.
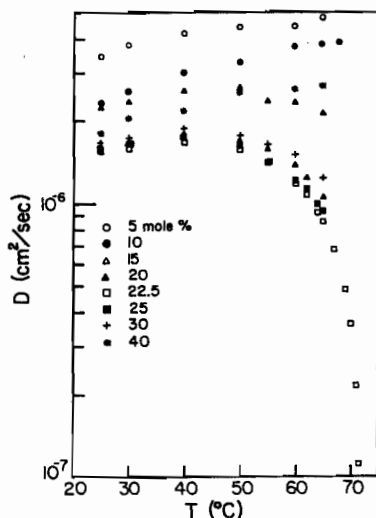
Figure 1. Mutual diffusion coefficient as a function of temperature for various concentrations of THF in water.

boiling point at 1-atm pressure for this mixture is roughly 64–65 °C (see Figure 5). The 22.5 mol % solution was studied up to liquid–liquid phase separation at 71.85 °C, the lower critical solution temperature (LCST), which is in the superheated (relative to boiling) regime.

The key quantity to be determined from the light scattering is the mutual diffusion coefficient of the concentration fluctuations, D. It is obtained from

$$D = \mu_1/2q^2 \tag{2}$$

where

$$q = \frac{4\pi n}{\lambda} \sin \theta/2 \tag{3}$$

and where $n = 1.38$ is the refractive index of the solutions and θ is the scattering angle. μ_1 was checked in initial experiments and found to have the expected q^2 dependence.

The viscosity was measured in a sealed Poiseuille flow viscometer with ~2-mL volume and capillary 15 cm long and 0.08 cm in diameter. Temperature control was achieved by immersing the viscometer in a circulating, temperature-controlled (±0.01 °C) water bath. Flow measurements were made with a stopwatch. Densities of the solutions necessary to convert kinematic to shear viscosity were determined gravimetrically by means of a 25-cm³ pycnometer. The error in the viscosity measurement was 1%.

III. Results

The mutual diffusion coefficients determined by the light scattering are given in Figure 1. D shows a strong decrease above 50 °C for concentrations between 20 and 30 mol % THF with the 22.5 mol % solution showing the smallest D and the fastest decrease. This concentration corresponds closely to the critical concentration at the LCST of the THF/H₂O mixture.[11] Nearby concentrations show nearly the same decrease with temperature, but more distant concentrations show very little effect. This decrease in D may be interpreted as critical slowing down of the concentration fluctuations as one approaches the LCST.

To show this critical phenomena effect in a stronger light, the effect of the viscosity, which also decreases with increasing temperature, can be removed. An estimate of the correlation length, ξ, of the concentration fluctuations can be obtained from D and the viscosity, η, by using the Stokes–Einstein relation[12]

$$D = k_B T/6\pi\eta\xi \tag{4}$$

(11) Matous, J.; Hrncirik, J.; Novak, J. P.; Sobr, J. *Collect. Czech. Chem. Commun.* **1970**, *35*, 1904.

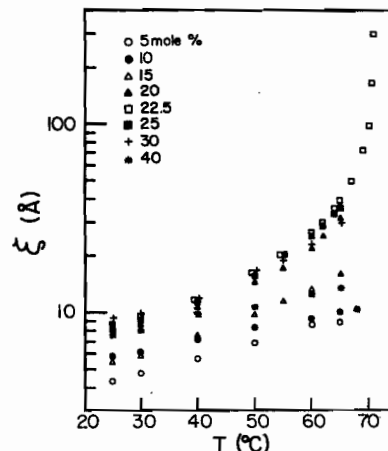(12) Czworniak, K. J.; Anderson, H. C.; Pecora, R. *Chem. Phys.* **1975**, *11*, 451.

Figure 2. Correlation length determined from the Stokes–Einstein relation as a function of temperature for various concentrations of THF in water.
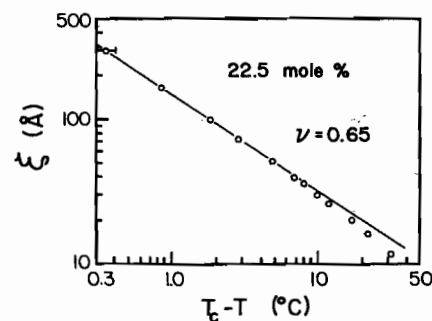

Figure 3. Correlation length as a function of temperature difference from the critical temperature for the 22.5 mol % THF solution. The straight line represents power-law behavior with exponent $\nu = 0.65$.

Figure 2 displays ξ vs T. Now all solutions show monotonic increases in ξ with increasing T, the largest increase in ξ occurring for the concentrations closest to the critical concentration. Furthermore, for concentrations between 20 and 30 mol % THF, the smallest correlation lengths are still ~8 Å, which is larger than the molecular size and hence implies molecular association.

Figure 3 tests the critical phenomena type behavior of the correlation length of the 22.5 mol % solution by plotting ξ vs $T_c - T$ where T_c is the LCST. Near a critical point it is expected that[13,14]

$$\xi = \xi_0 \left(\frac{T_c - T}{T_c}\right)^{-\nu} \tag{5}$$

Hence, the log–log graph in Figure 3 should be a straight line with slope $-\nu$. The graph is not perfectly linear although the limiting slope near $T_c - T \rightarrow 0$ is 0.65. This is in good agreement with the well-established value of $\nu = 0.63$ found to hold for binary liquid systems.[14] Thus, ξ derived from eq 4 is at least partially consistent with the critical phenomena analysis.

The nonlinearity in Figure 3 may be a result of a noncritical, background term that contributes to the light-scattered first cumulant. Equation 4, while instructive in the qualitative behavior of the correlation length, is valid only in the limit of no background. Since the relative background contribution is large far from the critical point, eq 4 could be a poor approximation for the measurements reported here.

The correct form for the diffusion coefficient is given by[15–17]

$$D = D_C + D_B \tag{6}$$

(13) Stanley, H. E. *Introduction to Phase Transitions and Critical Phenomena*; Oxford University Press: New York, 1971.

(14) Sengers, J. V.; Levelt Sengers, J. M. H. In *Progress in Liquid Physics*; Croxton, C. A., Ed.; Wiley: New York, 1978.

where

$$D_C = \frac{k_B T}{6\pi\eta\xi}\Omega(q\xi) \qquad (7)$$

and

$$D_B = \frac{k_B T}{16\eta_0\xi}\left[\frac{1 + q^2\xi^2}{q_c\xi}\right] \qquad (8)$$

D_C and D_B are the critical and background parts of the diffusion coefficient, $\Omega(x)$ is the Kawasaki function,[18] η_0 is the background viscosity, and q_c is a wavevector which controls the magnitude of the background. In general, analysis of PCS data is difficult far from the critical point because of the background term. However, for the analysis here eq 8 can be simplified by noticing that, with the experimental $q = 8.96\ \mu^{-1}$ and the largest $\xi = 300$ Å, the largest $q\xi = 0.27$; thus $q^2\xi^2 \ll 1$ and can be ignored. Next I use $\Omega(x \ll 1) = 1$, $\eta_0 \simeq \eta$ and is a weak function of T for $T_c - T > 1\ °C$, to find

$$D = \frac{k_B T}{6\pi\eta\xi}\left[1 + \frac{6\pi}{16q_c}\frac{1}{\xi}\right] \qquad (9)$$

Now combine this with eq 5 and with some rearrangement obtain

$$\frac{\eta D}{T t^\nu} = a + b t^\nu \qquad (10)$$

where $a = k_B/6\pi\xi_0$, $b = k_B/16q_c\xi_0^2$, and $t = (T_c - T)/T_c$.

The fit of the data to eq 10 can be obtained by using experimental values for D, η, T_c, and T and varying only ν until linearity is achieved. The intercept and slope, a and b, then yield ξ_0 and q_c. The data for the 22.5 mol % solution fit by eq 10 are given in Figure 4. The analysis is successful in that the linearity is sensitive to ν and a value of $\nu = 0.63 \pm 0.03$ is found, in good agreement with the accepted value.[14]

These results for the 22.5 mol % solution demonstrate that critical phenomena type fluctuations are indeed occurring in this solution and their effect is still relevant to the solution properties at 25 °C. Solutions not having this critical concentration can be made to display their critical phenomena behavior if the concept of the critical temperature is generalized. The required generalization is the pseudospinodal assumption[19,20] which has been used in the past to analyze off-critical-concentration data[19-21] and determine a critical region equation of state.[22] The pseudospinodal assumption states that any parameter which displays power-law behavior along the critical concentration isopleth as $T \rightarrow T_c$ will display the same behavior along any other concentration isopleth as $T \rightarrow T_s$, the pseudospinodal temperature. Thus, eq 5 becomes

$$\xi = \xi_0\left(\frac{T_s - T}{T_s}\right)^{-\nu} \qquad (11)$$

ξ_0 and ν are assumed to have the same values as along the critical concentration. The locus of T_s forms the pseudospinodal curve which is in the two-phase region. Obviously, $T_c = T_s$ at the critical concentration; otherwise at concentration x

$$|x - x_c| = B_s\left|\frac{T_c - T_s(x)}{T_c}\right|^\beta \qquad (12)$$

where $\beta \simeq 0.33$ is the critical exponent for the coexistence curve

(15) Oxtoby, D. W.; Gelbart, W. M. *J. Chem. Phys.* **1974**, *61*, 2957.
(16) Bhattacharjee, J. K.; Ferrell, R. A.; Basu, R. S.; Sengers, J. V. *Phys. Rev. A* **1981**, *24*, 1469.
(17) Burstyn, H. C.; Sengers, J. V. *Phys. Rev. A* **1982**, *25*, 488.
(18) Kawasaki, K. In *Phase Transitions and Critical Phenomena*; Domb, C., Green, M. S., Academic: New York, 1976; Vol. 5a.
(19) Benedek, G. B. In *Polarization Matiere et Rayonnement, Livre de l'honneur du Professor A. Kastler*; Presses de Universitaires de Paris: Paris, 1968.
(20) Chu, B.; Schoenes, F. J.; Fisher, M. E. *Phys. Rev.* **1969**, *185*, 219.
(21) Osman, J.; Sorensen, C. M. *J. Chem. Phys.* **1980**, *73*, 4142.
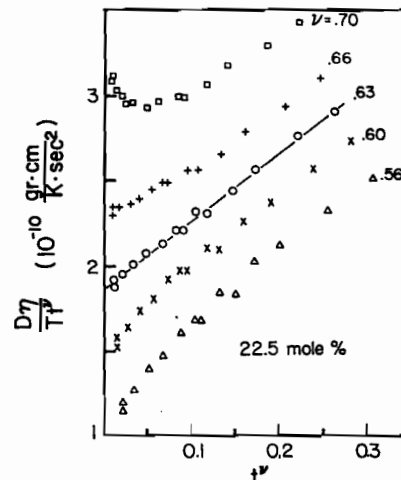(22) Sorensen, C. M.; Semon, M. D. *Phys. Rev. A* **1980**, *21*, 340.

Figure 4. Fit to eq 10 for the diffusion coefficient of the 22.5 mol % THF solution. The best straight line fit is obtained for a critical exponent of $\nu = 0.63$.
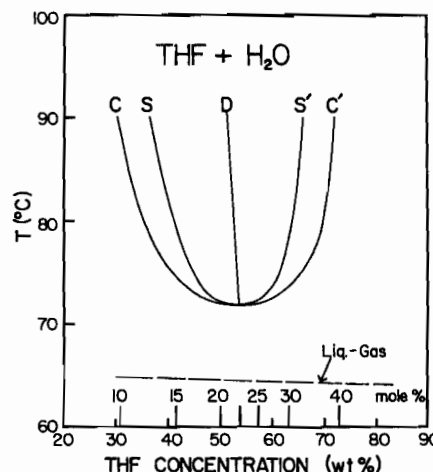

Figure 5. Phase diagram for the THF + water system. Curve CC' is the coexistence curve determined by Matous et al.[11] Curve SS' is the pseudospinodal curve as determined in the text. Line D is the coexistence curve diameter. Also shown is the equilibrium boiling point of the mixture at 1-atm pressure.

which has the same form as eq 12. The amplitude B_s has been found to have the value $0.63B$ from theoretical considerations[22] and $0.66B$ from empirical results,[21] where B is the amplitude of the coexistence curve.

I have used the pseudospinodal assumption to analyze the data not on the critical concentration. The pseudospinodal curve was determined from the coexistence curve for this system given by Matous et al.[11] Extraction of their data from their published graph led to $\beta = 0.33$ and $B = 127$ wt %, thus $B_s = 0.63B = 80$ wt %. The coexistence curve for this mixture is most symmetric when plotted versus weight percent concentration. The pseudospinodal was assumed to be symmetric with the coexistence curve diameter when plotted in this manner. The pseudospinodal and the coexistence curve are shown in Figure 5.

Values of $T_s(x)$ for $x = 15, 20, 25,$ and 30 mol % were determined from the graph in Figure 5. The concentrations $x = 5, 10,$ and 40 mol % did not have a value of T_s because the coexistence curve is a closed loop and a two-phase region does not occur at these concentrations. This is not a loss since the pseudospinodal assumption is not expected to be accurate too far from x_c. With the values of $T_s(x)$, the data could be fit to eq 10 in exactly the same manner as were the $x_c = 22.5$ mol % data. Unfortunately, lack of data close to T_s left the linearity very insensitive to the exponent ν; the graphs were quite linear for a wide range of ν. Thus, ν was held fixed at 0.63 and ξ_0 and q_c were
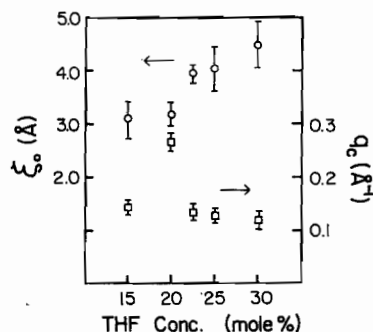
Figure 6. Parameters ξ_0 (circles) and q_c (squares) as a function of THF concentration determined from the fit to eq 10 with $\nu = 0.63$.

extracted from the fits. These results are shown in Figure 6.

Figure 6 shows a systematic trend in ξ_0 with concentration. This is not expected under the pseudospinodal assumption. A slight change in the symmetry of the pseudospinodal curve relative to the diameter, however, can yield values of ξ_0 equal, within error, for all x. Such a change is not otherwise warranted, however, and is not necessary for my purposes here. The fact that eq 10 and hence eq 5–8 are successful in describing the data with reasonably consistent ξ_0 values and $\nu = 0.63$ demonstrates that the LCST at 71.85 °C is seriously affecting the behavior of *all* these solutions not only near but quite far from the LCST.

IV. Discussion and Conclusion

The results above show that the liquid–liquid lower critical solution point in the superheated regime at 71.85 °C and 22.5 mol % THF gives rise to critical phenomena concentration fluctuations which are still active at 25 °C over a broad range of concentrations. Thus, the point to be made is that it is very likely that these critical fluctuations are responsible for the unusual properties of these solutions, such as sound absorbtion[9] and dielectric relaxation,[8] despite the rather large distance from the LCST.

One may now use the concepts of what drives these critical points in aqueous solutions to understand the molecular origins of the solution properties.[23] In complex liquid–liquid equilibrium systems one must consider the interplay of energy and entropy in the free energy expression to determine the equilibrium configuration. Thus at high temperatures, entropy, whose coefficient is the temperature, dominates and a binary system will mix due to the favorable entropy of mixing. As the temperature is lowered, energetic dislike of the molecules may eventually overwhelm the entropy and cause phase separation. In aqueous systems, water–solute hydrogen bonding may occur. This is energetically favorable but entropically disfavored because of the directional nature of the hydrogen bond and the consequent loss of configurational entropy. At yet lower temperatures, however, this configurational entropy loss can be negated by the energetically

favorable hydrogen bonding to cause the phase-separated liquids to remix. Finally, water–water hydrogen bonding may be more favorable than water–solute bonding. This may occur at even lower temperatures where the entropy loss due to the segregation of the water and solute molecules cannot keep the solution mixed. Under these conditions the system phase separates again.

According to this picture of critical points, in the THF + water system the lower critical solution point at 71.85 °C and 22.5 mol % THF must be due to THF–water hydrogen bonding. Thus, water–water hydrogen bonding, which may be interpreted as giving rise to clathrate-like structures, is probably not important in this system's properties for $T \geq 25$ °C. It would be interesting, however, to study this system at lower temperatures to see if evidence for a critical point could be found in this regime. Such a critical point would not be unexpected given water's propensity to self-associate at low temperatures.

In general, the THF + H_2O system is just one example of "distant" critical points affecting solution properties. As reviewed in the Introduction, the aqueous *tert*-butyl alcohol system displays effects from critical points both at the low-temperature end of an upper miscibility gap (hence above room temperature) and at the high-temperature end of a low-temperature miscibility gap (hence below room temperature).[3] These critical points are most likely due to alcohol–water and water–water hydrogen bonding, respectively. It is important to stress that the critical points need be neither nearby nor on the equilibrium phase diagram. Thus, for the THF + water system the LCST was above the equilibrium boiling point. In the *tert*-butyl alcohol + water system the high-temperature critical point is certainly not on the phase diagram but must be either salted out[24] or made to occur by addition of the isomer *sec*-butyl alcohol.[4] Recent sound absorbtion measurements in the system of 1-propanol and water, which is totally miscible in the equilibrium regime, also indicate the anomalous behavior can be interpreted as due to concentration fluctuations.[25] Despite the lack of phase transitions and critical points on the phase diagram of either the propanol or the butanol solutions, critical phenomena fluctuations can still occur and have a strong influence if they reside in some other direction than temperature or concentration (e.g., pressure or salt concentration) of the phase diagram. We have demonstrated this behavior in systems of 3-methylpyridine in H_2O/D_2O mixtures.[26]

Thus, it seems that a profitable point of view for future studies of unusual and anomalous properties of aqueous solutions is to look for critical points in the system or in the system perturbed in some way (salting, isomeric substitution, H_2O/D_2O exchange, pressure) to uncover hidden critical points. The distant effect of such points can cause fluctuations which affect the solution properties.

Registry No. THF, 109-99-9; H_2O, 7732-18-5.

(23) Hirschfelder, J. D.; Stevenson, D.; Eyring, H. *J. Chem. Phys.* **1937**, *5*, 896.

(24) Ludemann, H. D., private communication.
(25) Madigosky, W. M.; Warfield, R. W. *J. Chem. Phys.* **1987**, *86*, 1491.
(26) Larsen, G. A.; Sorensen, C. M. *Phys. Rev. Lett.* **1985**, *54*, 343. Sorensen, C. M.; Larsen, G. A. *J. Chem. Phys.* **1985**, *83*, 1835.