Chemical equilibrium in supercritical fluids: Solvent effects on the dimerization equilibrium constant

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(Received 16 November 2001; accepted 27 February 2002)

We study dimerization equilibrium between two dilute solutes in a supercritical solvent. Nonlocal hypernetted chain integral equation theory is employed to calculate the dimerization equilibrium constant for a wide range of solvent thermodynamic conditions and model potential parameters. The equilibrium constant displays a characteristic three-regime density dependence along near-critical isotherms, where it initially increases at low densities, decreases in the medium-density near-critical region, and increases again at high densities. The three regimes in the behavior of the equilibrium constant are discussed in terms of the energy-dominated low-density, desolvation-dominated medium-density, and entropy-dominated high-density regions. © 2002 American Institute of Physics. [DOI: 10.1063/1.1471553]

I. INTRODUCTION

Supercritical fluids (SCFs) are currently receiving much scientific and technological interest due to their unique physical properties, which combine certain advantageous features of both liquid and gas phases, e.g., liquidlike densities, gaslike viscosities, and diffusivities that are intermediate between typical gas and liquid values.1–6 The resulting combination of high dissolving power and enhanced mass-transfer rates makes SCFs attractive alternatives to conventional liquid solvents for such industrial applications as extraction, separation and reaction processes.3,7,8 In addition, the high compressibility of SCFs in the near-critical region allows one to tune their properties to desired values by applying small changes in pressure, which in turn makes it possible to tailor the rates, yields, and selectivities of chemical reactions.9–13

Chemical processes in SCFs can be controlled by a variety of factors, such as enhanced transport coefficients, increased reactant solubilities, facilitated separation, and strong thermodynamic pressure effect on the rate constants.9–13 For any given reaction, several aforementioned factors can be affecting the reaction rate simultaneously, which makes the analysis of chemical processes in SCFs rather involved.12–14 Therefore, it is important to study simple, well-defined reactions, where it is possible to isolate a few dominant factors influencing the reactivity. In this regard, the investigation of chemical equilibria in SCFs provides a particularly appealing area of research, since the values of the equilibrium constants are largely determined by the structural aspects of supercritical solvation.

Experimental studies of chemical equilibria in SCF solvents have been carried out for a wide variety of processes, including tautomeric and hydrogen bonding equilibria, as well as dimerization and isomerization reactions.15–27 One of the most thoroughly studied equilibrium chemical processes in SCFs is the dimerization of 2-methyl-2-nitrosopropane (MNP). Kimura and co-workers have measured the equilibrium constant for this reaction in several supercritical solvents (CO2, CHF3, CClF3, Ar, and Xe) across the whole solvent density range, from gas to liquid.15–18 It was found that in all solvents the density dependence of the equilibrium constant measured along near-critical isotherms displayed a characteristic S-shaped behavior. Specifically, the equilibrium constant increases with density in the low-density region, passes through a maximum somewhat below the solvent critical density, decreases with density in the compressible near-critical regime, passes through a minimum somewhat above the critical density, and then increases again in the high-density region.

Kimura et al. have proposed a qualitative interpretation of the observed “three-regime” density dependence of the equilibrium constant by invoking a crossover from the energy-dominated low-density to the packing-dominated high-density regime.17 According to their arguments, the solute–solvent attraction strength plays a dominant role in determining the density behavior of the equilibrium constant at low densities, which is confirmed by its strong temperature dependence in this regime. On the other hand, the structural properties of a dense fluid are almost entirely determined by the packing effects, and since the volume occupied by a dimer is smaller than that occupied by two monomers, an increase in pressure (or density) shifts the equilibrium towards the dimer formation, which is reflected in the increase of the equilibrium constant at high densities. Regarding the medium-density region, Kimura et al. attribute the observed decrease of the equilibrium constant with the solvent density to the “desolvation” effect.17 In particular, the highly compressible near-critical region is characterized by the largest local solvent density enhancement (relative to the bulk density) around an isolated solute. The formation of a dimer decreases the volume available to the solvent in the...
vicinity of the solute, which could lead to a negative density derivative of the equilibrium constant.

In order to provide a quantitative basis for the above interpretation, one needs to compute the solvent-mediated potential of mean force (PMF) between the two solutes (reactants). The equilibrium constant for the dimerization reaction can be expressed in terms of the solvent-mediated PMF evaluated at the dimer’s bond length.17 Kimura and coworkers have considered a simple model of two spherical solutes at infinite dilution in a fluid of spherical solvent molecules, and have calculated the solvent-mediated PMF from the integral equation theory of homogeneous fluids.17,28 However, it has been recently shown that such approach can produce grossly inaccurate results at near-critical conditions, to the extent that even the sign of the PMF can be given incorrectly.29 The failure of the homogeneous fluid approach stems from the fact that it does not account in a consistent way for the solute-induced solvent density inhomogeneities. A much more accurate description of the structural properties of dilute supercritical solutions is provided by an extended (nonlocal) version of the integral equation theory developed for nonuniform systems.30–32 This has been confirmed in our earlier study, where we have computed the PMF between two dilute solutes in a supercritical solvent both from Monte Carlo simulation and from the two versions of the hypernetted chain (HNC) integral equation theory—homogeneous and nonlocal.29 The nonlocal theory was found to be in excellent agreement with the simulation and to provide a very substantial improvement over its homogeneous counterpart.

An additional advantage of employing the nonlocal theory for the present problem is due to the fact that this approach operates explicitly with anisotropic solvent density profile induced by the two solutes. The accurate knowledge of the latter profile is crucial for calculating the configurational volume change in the course of a dimerization reaction.15 Kimura et al. have attempted to compute this profile from the solvent density profiles around isolated solutes by employing the Kirkwood superposition approximation, but have found that such approach was insufficient to explain the observed inverted density dependence of the dimerization equilibrium constant in the medium-density regime.15

In view of the above, the goal of the present work is to perform a theoretical study of supercritical solvent effects on the solute–solute PMF and dimerization equilibrium constant on the basis of nonlocal integral equation theory. In order to achieve this goal, our earlier study29 needs to be extended in several directions. First, the aforementioned study was limited to a single point on the solvent phase diagram, which was located in the near-critical region. In order to understand the observed “three-regime” density dependence of the equilibrium constant, it is necessary to perform extensive model calculations of the solute–solute PMF for a wide range of solvent thermodynamic conditions and model potential parameters. Second, our earlier work was largely limited to the analysis of the solvent effects on the contact and solvent-separated solute pairs, which are governed by the values of the solute–solute PMF at or beyond the contact separation of the two solutes. At the same time, the calculation of the dimerization equilibrium constant requires the knowledge of the solute–solute PMF at the dimer’s bond length, i.e., at the distances smaller than the contact separation. Hence, it is necessary to analyze the behavior of the solvent-mediated solute-solute PMF at separations corresponding to various degrees of overlap between the two solutes. Both these extensions of our earlier work form the subject of the present study.

The remainder of the paper is organized as follows: In Sec. II we specify our microscopic model and briefly review the calculation of the dimerization equilibrium constant from the nonlocal HNC integral equation theory. In Sec. III we perform extensive model calculations of the dimerization equilibrium constant for a wide range of solvent thermodynamic conditions and model potential parameters. The “three-regime” density dependence of the equilibrium constant is discussed in terms of energetic and entropic factors. In Sec. IV we conclude.

II. MICROSCOPIC MODEL AND THE CALCULATION OF THE EQUILIBRIUM CONSTANT

We consider the following simple model for a dimerization reaction in solution. Two dilute spherical solutes are in dimerization equilibrium in a solvent composed of spherical particles: \( 2M = D \), where \( M \) stands for a monomeric solute, \( D \) stands for a dimer, and \( K \) is the equilibrium constant for the dimerization process.17 This process is schematically depicted in Fig. 1.

We assume that the solvent particles interact through pairwise additive potential of the Lennard-Jones (LJ) form,

\[
\begin{align*}
    u_\ell(r) &= 4\epsilon \left[ \left( \frac{\sigma^6}{r^6} \right) - \left( \frac{\sigma^6}{r^6} \right)^{2/3} \right], \\
    u(r) &= 4\epsilon \left[ \left( \frac{\sigma^12}{r^6} \right) - \left( \frac{\sigma^6}{r^6} \right) \right].
\end{align*}
\]

where \( \epsilon \) is the potential well depth and \( \sigma \) is the effective diameter of the solvent particle.

The solute–solvent potential has the same form, but with different \( \epsilon \) and \( \sigma \) parameters,

In what follows, we will assume that the solute (monomer) diameter is given by \( \sigma_M = 2\sigma - \sigma_s \).

The direct (bare) solute–solvent interaction potential will be left unspecified, since its effect on the equilibrium constant is independent of the solvent, while our major interest here is in the supercritical solvent effects on the dimerization equilibrium constant. In order to isolate these effects, we focus on the ratio of the equilibrium constant to its gas-phase value, \( K/K_0 \), where \( K_0 = \lim_{\rho \to 0} K \), and \( \rho \) is the solvent bulk
number density. The ratio $K/K_0$ can be obtained directly from the excess (solvent-mediated) solute–solute PMF, $W(R)$, as follows:\textsuperscript{17} 
\[ \ln(K/K_0) = -\beta W(l), \] (3) 
where $\beta = 1/k_BT$ and $l$ is the bond length of the dimer molecule. Note that the above equation assumes that the dimer’s bond length has the same value in the gas phase and in the solution, which is a standard approximation in the studies of solvent effects on equilibrium constants.\textsuperscript{17}

The excess solute–solute PMF is given by the following exact relations:\textsuperscript{33} 
\[ W(R) = \int_R^\infty F(R')dR', \] (4) 
where the excess mean force, $F(R)$, is given by 
\[ F(R) = -\int d\mathbf{r}\mathbf{V}u(r)\rho_r(R). \] (5)

In the above, $\rho_r(R)$ is the conditional probability of finding the solvent particle at $r$ given that one solute is at the origin, and the other solute is located at $R$. 

In order to compute the solvent density profile $\rho_r(R)$, we employ the nonlocal HNC integral equation theory,\textsuperscript{29–32} 
\[ \rho_r(R) = \rho\exp\left[ -\beta\left( u(r) + u(|r-R|) + \mu^ex|_{\rho_r(R)} \right) \right. \] 
\[ -\mu^ex|_{\rho_r(R)} - \left( \rho_r(R) - \rho \right) \frac{\partial \mu^ex}{\partial \rho} \] 
\[ + \left. \int d\mathbf{r'}c(|r-r'|)(\rho_{r'}(R) - \rho) \right], \] (6) 
where $c(r)$ is the direct pair correlation function of the neat solvent, $\mu^ex|_{\rho}$ is the solvent excess chemical potential evaluated at the density $\rho$, and $\rho_r(R)$ is the weighted local density. The latter is obtained as a weighted average of the actual density profile over a microscopic volume determined by the range of the solvent pair potential, 
\[ \rho_r(R) = \int d\mathbf{r'}\rho_r(R')w(|r-r'|), \] (7) 
where $w(r)$ is the normalized weight function given by 
\[ w(r) = \frac{\exp(-\beta u^{rep}(r)) - 1}{4\pi \int_0^{2\pi} dr' \int_0^{\pi} d\theta' \exp(-\beta u^{rep}(r')) - 1}. \] (8) 
with $u^{rep}(r) = u_s(r) + \epsilon_s$ for $r \leq 2^{1/6}\sigma_s$, and $u^{rep}(r) = 0$ otherwise.

We remark in passing that if $\rho_r(R)$ is set to be equal to $\rho$, then Eq. (6) reduces to the homogeneous HNC expression for the anisotropic solvent density profile.\textsuperscript{34} In the presence of significant solute-induced solvent density inhomogeneities, the weighted local density deviates substantially from the bulk value, and the result for $\rho_r(R)$ given by the nonlocal theory is very different from the homogeneous theory result.\textsuperscript{29}

In order to solve Eq. (6), one needs to compute $c(r)$ and $\mu^ex$ for the neat solvent. In the present work, $c(r)$ is obtained by solving the Ornstein–Zernike (OZ) equation,\textsuperscript{35} 
\[ h(r) = c(r) + \rho \int d\mathbf{r}'c(|r-r'|)h'(r'), \] (9) 
coupled with the HNC closure, 
\[ h(r) = \exp[-\beta u_s(r) + h(r) - c(r)], \] (10) 
where $h(r)$ is the solvent total correlation function. The solvent excess chemical potential in the HNC approximation is given by\textsuperscript{36} 
\[ \mu^{ex} = 4\pi k_BT \int_0^{\infty} dr^2 \left[ (h(r)(h(r) - c(r))/2 - c(r)) \right]. \] (11)

Substituting $c(r)$ and $\mu^{ex}$ obtained from Eqs. (9)–(11) in Eq. (6), one can calculate $\rho_r(R)$ through an iterative procedure, and then compute the excess solute–solute PMF from Eq. (4) and the dimerization equilibrium constant from Eq. (3). In the next section, we specify our model potential parameters and perform extensive model calculations of the excess PMF and the equilibrium constant.

III. MODEL CALCULATIONS OF THE DIMERIZATION EQUILIBRIUM CONSTANT

We start by performing model calculations of the excess solute–solute PMF. We define dimensionless solvent density and temperature in terms of the solvent LJ parameters as follows: $\rho^* = \rho\sigma_s^3$, and $T^* = k_BT/\epsilon_s$. The best estimates for the critical density and temperature of a LJ fluid are: $\rho^c = 0.316$ and $T^* = 1.312$.\textsuperscript{27} In view of the pronounced “three-regime” density dependence of the dimerization equilibrium constant observed experimentally, we consider the following three state points on the solvent phase diagram: $(\rho^* = 0.1, T^* = 1.325)$, $(\rho^* = 0.3, T^* = 1.325)$, and $(\rho^* = 0.7, T^* = 1.325)$, which represent low-, medium-, and high-density regions, respectively. All three points are located on the near-critical isotherm $T^* = 1.325$, which corresponds to the reduced temperature $T_r = T/T_c = 1.01$, i.e., this isotherm lies 1% above the solvent critical point.

It is worth pointing out that we define reduced temperature and density in terms of the simulation critical point of LJ fluid,\textsuperscript{27} while we treat the bulk solvent in the HNC approximation, which does not possess a true critical point, but only a maximum in compressibility.\textsuperscript{38} This is clearly an approximation. In order to check its accuracy, we have performed several representative calculations with the chemical potential obtained from the LJ equation of state\textsuperscript{39} (as given by the simulation) and the solvent direct correlation function computed from the hierarchical reference theory,\textsuperscript{40} which produces critical point for LJ fluid in good agreement with the simulated one. The results of these calculations were very close to the results obtained within the HNC treatment of the bulk solvent, and the latter approach will be utilized through the remainder of the paper.

We compute the excess PMF for two dilute solutes, whose diameter is taken to be twice as large as the solvent diameter: $\sigma_m/\sigma_s = 2$, which yields for the solute–solvent size parameter: $\sigma/\sigma_s = 1.5$. Since there exists a substantial experimental evidence\textsuperscript{17,18} that the solute–solvent interaction strength plays a particularly important role in determining
the density dependence of the dimerization equilibrium constant, we consider three model systems with the following values of the solute–solute potential well-depth, \( e/\varepsilon_s = 1, 1.41, \) and 1.73.

The results of our calculations of \( W(R) \) for three model systems at three thermodynamic state points are displayed in Fig. 2. One immediately sees that the increase of the solute–solvent interaction strength has a completely different effect on the excess solute–solute PMF in the three density regimes. At the low-density point, increasing \( \epsilon \) stabilizes the excess PMF for all solute–solute separations, including solvent-separated and contact solute pairs, as well as smaller separations, which correspond to the overlap of the two solutes and the formation of a dimer. It follows from Eq. (3) that increase of the solute–solvent interaction strength enhances the dimerization equilibrium constant in the low-density regime. This behavior can be understood by noting that the solvent molecules located in the vicinity of the overlap of the two solutes can experience an attractive interaction with both particles forming the dimer. At the same time, the local solvent density around isolated solutes is sufficiently low, so that formation of a dimer is not accompanied by desolvation process. As a result, at low densities dimerization is energetically favorable (see also below), and is enhanced for larger values of the solute–solvent interaction strength.

By contrast, at the high-density point, the solvation shells of isolated solute molecules are largely filled, and the formation of a dimer requires the loss of several nearest neighbors by each of the solutes. This desolvation effect becomes more pronounced for stronger solute–solvent interactions. Indeed, one can see from the upper panel of Fig. 2 that at the high-density point the increase of \( \epsilon \) destabilizes \( W(R) \) for all solute–solute separations, and therefore leads to a decrease in the dimerization equilibrium constant.

Regarding the medium-density point, the effect of the solute–solvent interaction strength on the excess PMF is rather complicated. One can see from the middle panel of Fig. 2 that the solvent-separated solute pair is stabilized for all three systems, and the stabilization is enhanced for larger values of \( \epsilon \). At the same time, the contact pair is destabilized, and its destabilization increases with \( \epsilon \). (We remark in passing that this behavior of the excess PMF has been already discussed in our earlier study.\(^{29}\)) As for the smaller solute–solute separations, which correspond to the formation of a dimer, the effect of \( \epsilon \) on \( W(R) \) and the dimerization equilibrium constant depends sensitively on the value of the dimer’s bond length. For the particular model system considered here, for bond lengths smaller than 1.5\( \sigma_s \), the dimerization is enhanced by stronger solute–solvent interaction, while for larger bond lengths the situation is reversed.

Having discussed the behavior of the excess solute–solute PMF in the three density regimes, we now turn to the analysis of the density dependence of the dimerization equilibrium constant. We choose the following set of the solute–solvent model potential parameters, \( e/\varepsilon_s = 1.41, \sigma/s = 1.5, \) and set the dimer’s bond length to be \( l = 0.93\sigma \) (in terms of the solute diameter, the latter value yields \( l = 0.7\sigma_M \), which roughly corresponds to the bond length of the MNP dimer in terms of the effective diameter of the MNP monomer.\(^{17}\) We will consider the effect of changing the bond length on the equilibrium constant below). For the above values of the model parameters, we compute the dimerization equilibrium constant as a function of the solvent density along the supercritical isotherm \( T^*=1.4 \), which corresponds to the reduced temperature \( T_r=1.07 \). Our results for \( \ln(K/K_0) \) as a function of the reduced solvent density \( \rho_r = \rho/\rho_s \) are shown in the upper panel of Fig. 3. One sees that the dimerization equilibrium constant displays the same S-shaped behavior, as was observed by Kimura et al. in their experimental studies of MNP dimerization in supercritical solvents.\(^{17}\) Specifically, \( \ln(K/K_0) \) initially increases at low densities, passes through a maximum around \( \rho_r=0.65 \), decreases with density, passes through a minimum around \( \rho_r=1.3 \), and increases again in the high-density region.

We now discuss the origins of the three regimes in the density dependence of the equilibrium constant. As already mentioned, the low-density behavior of \( K \) is largely determined by the energetic factors. As the solvent density is increased starting from zero, the number of “doubly bound” solvent molecules (i.e., molecules located in the vicinity of the overlap of the two solutes) also increases. This leads to the initial increase of the dimerization equilibrium constant with density. In order to illustrate the energy gain due to the formation of the dimer, we compute the following quantity:

\[
\Delta E_{\text{dim}} = \int dr\rho(r;R)(u(r)+u(|r-R|)) - 2\int dr\rho_0(r)u(r),
\]

(12)
where \( \rho_0(r) = \lim_{R \to \infty} \rho(r; R) \) is the (spherically symmetric) solvent density profile around an isolated solute, and in the first term we set \( |R| = l \). Our results for \( \Delta E_{\text{dim}} \) as a function of \( \rho_s \) are shown in the middle panel of Fig. 3. One sees that the energy gained due to dimerization initially increases with density, but around \( \rho_s = 0.6 \) it starts to decrease, and beyond \( \rho_s = 1.2 \) the formation of the dimer becomes energetically unfavorable. This is due to the fact that at higher densities the dimerization is accompanied by the loss of a part of the solvation shell where the two solutes overlap. This desolvation effect more than offsets the energy gains due to the doubly bound solvent molecules.

It is clear from the above discussion that purely energetic considerations cannot explain the increase of the dimerization equilibrium constant with \( \rho \) in the high-density regime. This increase is due to the entropic effects, since the more compact dimer occupies less volume than two monomers. This can be confirmed by computing the configurational volume change in the course of dimerization, \( \Delta V_{\text{dim}} \), which can be obtained from the monomer- and dimer-induced solvent density profiles as follows:

\[
\Delta V_{\text{dim}} = \frac{1}{\rho} \int d\mathbf{r} (\rho - \rho(r; R = l)) - \frac{2}{\rho} \int d\mathbf{r} (\rho - \rho_0(r)).
\]

(13)

The above equation expresses the configurational volume change as the difference in the excluded volumes corresponding to the immersion of a dimer and two monomers in the solvent.\(^{15}\)

It is worth pointing out that the configurational volume change contains both energetic and entropic effects, which enter through the solvent density profiles. The latter are largely determined by the energetic factors in the low-density limit and by the packing effects at high densities. As a result, \( \Delta V_{\text{dim}} \) by itself is sufficient to determine the density derivative of the equilibrium constant at all densities, as can be seen from the following exact thermodynamic relation:

\[
\Delta V_{\text{dim}} = -\kappa_T \rho k_B T \frac{\partial \ln K}{\partial \rho},
\]

(14)

where \( \kappa_T \) is the solvent isothermal compressibility. The above expression shows that negative configurational volume change corresponds to increase of the equilibrium constant with density, while positive \( \Delta V_{\text{dim}} \) corresponds to decrease of \( K \) with \( \rho \).

Our results for \( \Delta V_{\text{dim}} \) as a function of \( \rho_s \), are displayed in the lower panel of Fig. 3. We have computed \( \Delta V_{\text{dim}} \) both from the exact thermodynamic relation given by Eq. (14) (with \( \kappa_T \) obtained from the LJ equation of state given by the simulation\(^{19}\)) and from the approximate relation based on excluded volumes given by Eq. (13). One sees that the two methods of calculating the configurational volume change agree well with each other, especially in the near-critical region. In agreement with the density behavior of \( \ln(K/K_0) \), the configurational volume change is negative both at low densities (below \( \rho_s = 0.65 \)) and at high densities (above \( \rho_s = 1.3 \)). As already pointed out, the low-density increase of \( \ln(K/K_0) \) can be rationalized entirely in terms of the energetic gains in the course of the dimerization process, as reflected by increasingly negative \( \Delta E_{\text{dim}} \) at low \( \rho \). On the other hand, this explanation is not sufficient at high densities, where it is necessary to invoke the entropic effects, which produce negative \( \Delta V_{\text{dim}} \) and the concomitant increase of \( \ln(K/K_0) \) with \( \rho \) (even though \( \Delta E_{\text{dim}} \) is becoming increasingly positive in this regime).

Regarding the medium-density region, one observes from the middle panel of Fig. 3 that the energy gain due to the dimerization process decreases with the solvent density in this regime. At the same time, the bulk and local densities are not sufficiently high to make the entropic effects dominant. Indeed, the configurational volume change takes positive and large (due to high compressibility) values in this regime (it is worth reiterating that positive \( \Delta V_{\text{dim}} \) cannot be obtained within the homogeneous isotropic integral equation approach combined with the Kirkwood superposition approximation\(^{15}\)). Concomitantly, the dimerization equilibrium constant decreases with \( \rho \) at medium densities. As already mentioned in the Introduction, this can be attributed to the desolvolation effect. The highly compressible near-critical regime is characterized by large excess local densities around isolated monomers, and the formation of the dimer is accompanied by substantial desolvation. In the absence of significant entropic gains, this leads to the shift in the dimerization equilibrium towards the dissociation of the dimer with increasing density.

So far, we have focused on the density dependence of the dimerization equilibrium constant along a particular supercritical isotherm. It is also of interest to analyze its temperature dependence. To this end, we compute \( K \) for the same system as above \( (\epsilon/\epsilon_s = 1.41, \sigma/\sigma_s = 1.5, \text{ and } l = 0.93\sigma) \) along the following three isotherms: \( T^* = 1.325, 1.4, \text{ and } 2.5 \), which correspond to the reduced temperatures \( T = 1.01, 1.07, \text{ and } 1.91 \), respectively. Our results for \( \ln(K/K_0) \) as a

FIG. 3. Upper panel: \( \ln(K/K_0) \) vs \( \rho_s \), at \( T^* = 1.4 \). Middle panel: \( \Delta E_{\text{dim}} \) vs \( \rho_s \), at \( T^* = 1.4 \). Lower panel: \( \Delta V_{\text{dim}} \) vs \( \rho_s \), at \( T^* = 1.4 \), solid line is from Eq. (13) and dashed line is from Eq. (14).
function of the reduced solvent density are shown in Fig. 4. One sees that the S-shaped density dependence of the equilibrium constant becomes less and less pronounced with increasing temperature, and completely disappears at the highest temperature studied, where $K$ increases monotonically with density. Once again this behavior is consistent with the observations reported by Kimura et al. in their study of MNP dimerization.\(^\text{18}\) One can also note that the changes in the density dependence of the equilibrium constant with temperature reflect different physical origins of the three regimes in the behavior of $K$ discussed above. In particular, the slope of $\ln(K/K_0)$ as a function of density displays a strong temperature dependence in the low-density regime, while at the highest densities it is essentially independent of temperature. This is consistent with the fact that the behavior of $K$ is energy-dominated at low densities and entropy-dominated at high densities. Specifically, in the low density limit, the solute-induced solvent density profile is given by a Boltzmann-type expression, and the height of the first peak of the profile increases exponentially with inverse temperature. This results in a steeper density dependence of the equilibrium constant at lower temperatures. On the other hand, the solvent density profile at high densities is largely determined by packing effects, and the temperature dependence of the density slope of $\ln(K/K_0)$ is rather weak. As far as the medium-density region is concerned, the excess local solvent density induced by the solutes decreases with increasing temperature (as one moves away from the near-critical region). This leads to the weakening of the desolvation effect and the concomitant disappearance of the S-shaped density dependence of the dimerization equilibrium constant.

Having analyzed the dependence of the equilibrium constant on the solvent thermodynamic conditions, we next discuss its variation with the model potential parameters. As already mentioned in our discussion of the excess solute–solvent PMF, one of the most important parameters for the present problem is the solute–solvent interaction strength.

Hence, we consider the following three model systems: $\varepsilon/\varepsilon_s = 1, 1.41, 1.73$, with the solute–solvent size parameter and the dimer’s bond length taken to be $a/a_s = 1.5$ and $l = 0.93a$, respectively. We compute the dimerization constant as a function of solvent density along the supercritical isotherm $T^* = 1.325$ ($T_r = 1.01$). Our results for $\ln(K/K_0)$ versus $\rho_r$ are displayed in Fig. 5. Once again, the results illustrate the energy-dominated nature of the low-density regime, where the density slope of $\ln(K/K_0)$ increases dramatically with the solute–solvent interaction strength, and the entropy-dominated nature of the high-density regime, where the density slopes of $\ln(K/K_0)$ for all three model systems are roughly the same. One also sees that the S-shaped density dependence of $K$ becomes less pronounced for weaker solute–solvent interaction. This is due to the fact that less attractive solutes induce smaller local solvent density enhancements, which makes the desolvation effect at near-critical conditions less pronounced. It is interesting to note that for the set of model parameters considered, all three curves for $\ln(K/K_0)$ cross in one point, around the solvent critical density. Below this density, the increase in the solute–solvent interaction strength favors the formation of the dimer due to increasing energy gain in the dimerization process. Above this density, the trend is reversed due to stronger desolvation effect for more attractive solutes. We note that all the above observations are consistent with the general trends in the behavior of the excess solute–solvent PMF illustrated for these three model systems in Fig. 2.

Another important parameter governing the density dependence of the dimerization equilibrium constant is the solute/solvent size ratio. In order to analyze its effect on $K$, we consider the following three model systems: $a/a_s = 1, 1.5, 2$, with the solute–solvent well depth and the dimer’s bond length taken to be $\varepsilon/\varepsilon_s = 1.41$ and $l = 0.93a$, respectively (note that the above choice of $a/a_s$ corresponds to the solute/solvent size ratios $a_M/a_s = 1, 2, 3$, respectively).
tively). We compute the dimerization constant as a function of solvent density along the supercritical isotherm $T^* = 1.325$. Our results for $\ln(K/K_0)$ versus $\rho_s$ are displayed in Fig. 6. Unlike the solute–solvent interaction strength and the solvent temperature, the solute/solvent size ratio effects the density slope of $\ln(K/K_0)$ in all three density regimes. One sees that the steepest increase of the equilibrium constant with density is observed for the largest solute both in the low-density and in the high-density limit. The former reflects the enhanced energy gain in the dimerization process due to the increase in the solute–solvent interaction range, while the latter reflects the enhanced entropic gain in the formation of the dimer due to the increase in the geometric volume of the solute–solute overlap. The largest solute is also associated with the strongest desolvation effect, which results in the most pronounced S-shaped density dependence of the dimerization equilibrium constant.

Lastly, we analyze the effect of the dimer’s bond length on the density dependence of the equilibrium constant. We set $\epsilon'/\epsilon_s = 1.41$ and $\sigma'/\sigma_s = 1.5$, and consider three model systems with $l = 0.93\sigma$, $1.07\sigma$, and $1.2\sigma$, respectively (in terms of the solute diameter, these values correspond to bond lengths $l = 0.7\sigma_M$, $0.8\sigma_M$, and $0.9\sigma_M$, respectively). We compute the dimerization constant as a function of solvent density along the supercritical isotherm $T^* = 1.325$. Our results for $\ln(K/K_0)$ versus $\rho_s$ are displayed in Fig. 7. One sees that throughout the entire density range the dimerization equilibrium constant decreases with increasing bond length. This simply reflects the fact that in the range of $l$ values considered, the excess solute–solvent PMF is a monotonically increasing function of the solute–solvent separation in all three density regimes, as was illustrated earlier in Fig. 2. In the high-density regime, this is due to the decreasing volume of the solute–solvent overlap, while in the low-density regime this is due to the decreasing energy gain experienced by the doubly bound solvent particles, which are positioned further away from the two centers of attraction for dimers with larger bond lengths.

IV. CONCLUSION

In this work we have studied the supercritical solvent effects on the excess solute–solute PMF and the dimerization equilibrium constants. We considered a simple microscopic model involving two dilute spherical solutes in a fluid of spherical solvent particles. Nonlocal HNC integral equation theory was employed to compute the excess solute–solute PMF and the equilibrium constants.

The calculations were performed for a wide range of solvent thermodynamic conditions and model potential parameters. It was found that the dimerization equilibrium constant displays a characteristic S-shaped density dependence along near-critical isotherms, provided the solute–solvent interaction strength and the solute/solvent size ratio are both sufficiently large. The three regime density behavior of the equilibrium constant becomes less pronounced at higher temperatures and/or for smaller/less attractive solutes.

We have discussed the three regimes in the behavior of the equilibrium constant in terms of the energy-dominated low-density, desolvation-dominated medium-density, and entropy-dominated high-density regions. In order to provide a quantitative basis for the above interpretation, we have computed energy and configurational volume changes associated with the dimerization process from the monomer- and dimer-induced anisotropic solvent density profiles provided by the nonlocal HNC theory.

All qualitative features in the behavior of the dimerization equilibrium constant found in our work are in agreement with the trends observed in the experimental studies of MNP dimerization in various supercritical solvents.15–18 We have not attempted to perform a quantitative comparison between theory and experiment, since the simple isotropic LJ potential employed in the present study is not sufficient to describe
the interaction between a MNP monomer and solvent particles, where a directional anisotropic interaction due to the MNP nitroso group can play an important role. A more realistic potential model is needed in order to analyze the experimental data. This will be the subject of our future research.

ACKNOWLEDGMENTS

S.A.E. acknowledges financial support from the Jeffress Memorial Trust (Grant No. J-650) and Chemistry Department of the University of Virginia. E.R. acknowledges financial support from the United States–Israel Binational Science Foundation (Grant No. 9900008), from the Bergman Memorial Research Grant, and from the Israeli Council of Higher Education (Alon fellowship).

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