

Near-criticality in dilute binary mixtures: Distribution of azulene between coexisting liquid and vapor carbon dioxide

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The equilibrium distribution of dilute solutes between vapor and liquid coexisting phases of near-critical solvents exhibits a simple dependence on the solvent's liquid density which extends over a wide temperature range; however, theory predicts this dependence only as an asymptotic limit. In order to test quantitatively the extension of this behavior and compare it with the value predicted from the asymptotic relationship, a novel high-pressure apparatus with a sampling manifold, which avoids perturbing the system during sampling, was used to measure the equilibrium concentrations of azulene in coexisting liquid and vapor carbon dioxide contained in a high pressure sapphire cell. The density and composition of the two phases under equilibrium were determined between 283 and 301 K. The linearity of $RT \ln K_D$ (K_D being the distribution equilibrium constant) in the solvent's liquid density was verified over the entire experimental temperature range, and the value of the slope was close to that corresponding to the asymptotic description as calculated with the hydrostatic hypernetted chain theory. An explanation for this observation lies in the weak temperature dependence of the Krichevskii function for this system; however a full quantitative description of the observed phenomenon remains a challenge, which should be provided by crossover theory. © 2002 American Institute of Physics. [DOI: 10.1063/1.1480862]

I. INTRODUCTION

The possibility of describing the properties of dilute solutions over a wide range of the fluid solvent thermodynamic states, covering the liquid, the gas and the supercritical solvent, is of increasing interest to understand solvation phenomena and to use supercritical fluids in several chemical processes.^{1,2} In order to achieve this goal it is important to be able to include in the general description the peculiar behavior observed in the near-critical region. In this thermodynamic region the solvent's enhanced response functions, i.e., isobaric heat capacity and isothermal compressibility, are coupled with solute-solvent interactions to produce a dependence of the properties of the infinitely dilute solute on temperature and on the solvent density ρ_1 which is different from that observed far from the solvent's critical point.³⁻⁶

Japas and Levelt Sengers⁷ derived the asymptotic linear dependence on the liquid phase density which governs the distribution of solutes between the coexisting liquid and va-

por phases of a solvent as it approaches its critical temperature T_c . This was an important contribution towards understanding the behavior of dilute solutions under near-critical conditions, particularly because it is difficult to explore experimentally the region close to T_c , where the fluid density changes strongly as the critical point is approached. Japas and Levelt Sengers also noted that the linear behavior was observed to extend more than 100 K from T_c , much more than expected for an asymptotic behavior. This feature has been frequently verified,^{8,9} especially for aqueous solutions, for which the majority of the experimental studies of solubility or distribution of solute between near-critical liquid-vapor phases exist. An exception to the extended linear behavior is the distribution of heavy water between coexisting liquid and vapor H₂O; the short linear region found for this system has been explained in terms of the almost ideal behavior of the mixture.¹⁰

In the study of near-critical binary dilute solutions it is customary to classify solutes as repulsive or attractive, an alternative denomination is volatile and nonvolatile.^{11,12} This classification makes reference to the relative strength of solute-solvent interactions when compared with the solvent-solvent intermolecular interactions. The majority of the binary systems for which an extended linear region has

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been reported contained volatile or repulsive solutes, and the greatest volume of data is for aqueous solutions. The properties usually determined in the experimental studies are related to the solutes' chemical potential at infinite dilution expressed either as Henry's constant k_H or as the distribution equilibrium constant of solute between liquid and vapor solvent K_D . Moreover, for solutions of gaseous solutes k_H and K_D are calculated from the equilibrium composition of the fluid phases. The calculation procedure, when used in the near-critical region, is not free from assumptions, which are necessary to enable the determination of these constants. In spite of careful data treatment,^{9,13} often there is no direct access to the value of these constants; hence it is always possible that the observed extended linear behavior for $\ln k_H$ and $\ln K_D$ could be influenced by the assumptions made in the calculation procedure.

An exception to the more frequently studied binary systems is the recent determination of the equilibrium distribution constant K_D of boric acid between water and steam up to 3.4 K below the solvent's critical point,¹⁴ i.e., up to a reduced temperature of $T_{\text{red}} \equiv (T/T_c) = 0.9947$. For this system, which contains an attractive solute, the plot of $T \ln K_D$ was also found to be linear in the liquid's density over a range 120 K wide. However, in this system the high critical temperature and pressure of water is a serious limitation to the precision of the determinations.

In the present work we report the results of a very careful study of the concentration of another attractive solute, azulene, in the coexisting liquid and vapor phases of near-critical CO_2 . The 25 K range of temperatures that has been covered extended between 278.17 K and 303.80 K, a range of T_{red} going from 0.9146 to 0.9989.

The paper is organized as follows. In Sec. II we present the thermodynamic relations which characterize the near-critical behavior and the asymptotic law. In Sec. III details of the experimental method are given, in Sec. IV the results obtained are presented. Section V is dedicated to a discussion of the results in the context of other studies.

II. THERMODYNAMIC RELATIONS AND ASYMPTOTIC LAW

The behavior of fluids close to a critical point is most conveniently described in terms of the Helmholtz energy A of the fluid.^{7,15} For a binary solution A_x , the derivative of the Helmholtz energy with respect to the solute's mole fraction x is

$$A_x = \mu_2 - \mu_1, \quad (1)$$

where μ_i is the chemical potential of the solvent (subscript 1), or of the solute (subscript 2); thermodynamic variables are used as subscripts to indicate partial derivatives of the functions with respect to those variables. The mole fraction of the solute in the liquid phase is denoted by x and in the coexisting vapor by y . Dilute solutions in near-critical solvents which are in the concentration range in which Henry's law is valid are of the greatest interest because they give access to the standard thermodynamic variables at infinite dilution, so we shall circumscribe our analysis to solutes in

this standard state. From Eq. (1) the pressure and temperature derivatives of A_x for a solute at infinite dilution can be calculated, they are¹²

$$V_2^\infty - V_1^* = V_1^* \kappa_T^* \left(\frac{\partial p}{\partial x} \right)_{T,V}^\infty, \quad (2)$$

where κ_T^* is the isothermal compressibility of the pure solvent. For the temperature derivative we have

$$S_2^\infty - S_1^* = -A_{x,T} + V_1^* \alpha_p^* \left(\frac{\partial p}{\partial x} \right)_{T,V}^\infty, \quad (3)$$

where α_p^* is the isobaric expansion coefficient of the pure solvent. Both equations show clearly that V_2^∞ and S_2^∞ will diverge at the solvent's critical point, the sign of the divergence will depend on the sign of $J = (\partial p / \partial x)_{T,V}^\infty$, the Krichevskii function, at the solvent critical point. For $J > 0$ the solute is repulsive or volatile, and for $J < 0$ it is attractive or nonvolatile.

For the coexisting liquid and vapor phases we have from Eq. (1),

$$A_x = A_y. \quad (4)$$

Taking into account that the Helmholtz energy may be divided into an ideal term and a residual term,¹⁶ $A = A^{\text{id}} + A^r$ it is possible to write for the binary solution at infinite dilution under the condition of coexistence of both fluid phases,

$$\lim_{x \rightarrow 0} RT \ln \frac{y}{x} \equiv RT \ln K_D = A_x^{r,\infty} - A_y^{r,\infty}, \quad (5)$$

Eq. (5) also gives the definition of the distribution equilibrium constant K_D of the solute between the liquid and the vapor phases.

Japas and Levelt Sengers used a classical Taylor series expansion to express A_x and A_y around the solvent's critical point and related them to $\ln K_D$,⁷ they did it in terms of the variables $(\delta T, \delta V^L, x)$, where V^L is the molar volume of the liquid phase and δ denotes the difference between the value of a variable and its value at the critical points, e.g., $\delta T = T - T_c$; an equivalent expression was used for A_y in the vapor phase. We preferred to expand the function $\Psi \equiv (A/V)$ in terms of $(\delta T, \delta \rho, \rho_2)$, where ρ is the fluid density of the mixture and $\rho_2 = x\rho$ the moles of solute per unit volume. The resulting expansion is

$$RT \ln K_D = \Psi_{\rho_2 \rho}^{c,r} (\delta \rho^L - \delta \rho^V) + \frac{\Psi_{\rho_2 \rho T}^{c,r}}{2} (\delta \rho^L - \delta \rho^V) \delta T + \frac{\Psi_{\rho_2 \rho \rho}^{c,r}}{2} [(\delta \rho^L)^2 - (\delta \rho^V)^2] + \dots \quad (6)$$

The superscript c indicates the value of the superscripted coefficient at the solvent's critical point. In order to write the coefficients of the three lower-order terms it is convenient to use the Krichevskii function which is also related to the Helmholtz energy because $J \equiv (\partial p / \partial x)_{V,T}^\infty = -A_{xV}$. J is not strongly affected by the vicinity of the solvent's critical point, hence it is a very adequate function to represent the thermodynamic behavior of dilute solutions, moreover it has

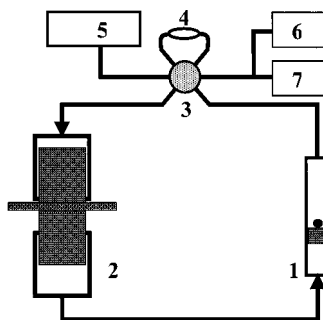


FIG. 1. Experimental apparatus. 1 sapphire cell with piston and stirrer; 2 coupled pumps; 3 six-way valve; 4 loop; 5 sampling manifold; 6 positive displacement pump; 7 carbon dioxide reservoir.

a direct connection with structural properties of the solution.^{17,18} The coefficients of Eq. (6) are then

$$\Psi_{\rho_2\rho}^{c,r} = \frac{J^c}{\rho_c^2},$$

$$\Psi_{\rho_2\rho T}^{c,r} = \frac{J_T^c}{\rho_c^2},$$

$$\Psi_{\rho_2\rho\rho}^{c,r} = \frac{1}{\rho_c^2} \left(J_\rho^c - \frac{2J^c}{\rho_c} \right).$$
(7)

The asymptotic limiting expression can be given in terms of the density of the liquid phase ρ^L , this leads to^{7,13}

$$RT \ln K_D = \frac{2J^c}{\rho_c} (\rho^L - \rho_c).$$
(8)

Japas and Levelt Sengers showed⁷ that this equation represents the asymptotic behavior also for nonclassical critical behavior. It is often observed that the linearity of $T \ln K_D$ with $(\rho^L - \rho_c)$ extends over more than 100 K from T_c for aqueous solutions of repulsive^{7,9,18} and attractive¹⁴ solutes. Phase equilibrium studies of the same binary systems sometimes also provide values of J^c , the Krichevskii parameter; the two values of J^c are close, but the agreement is not always quantitative. This was a strong incentive to measure directly K_D for an attractive solute dissolved in CO_2 , a solvent that does not require as high pressure and temperature conditions as is the case with water, in order to study the near-critical region.¹⁹

III. EXPERIMENT

Figure 1 shows a block diagram of the experimental apparatus used to study the partition coefficient of azulene in carbon dioxide. The details of this apparatus will be published elsewhere.²⁰ The core of the apparatus is the variable volume cell 1, consisting of a sapphire tube (external diameter 15 mm, internal diameter 10 mm, length 150 mm) provided with a piston which separates the carbon dioxide–azulene two-phase mixture (above the piston in the drawing) from a pressurizing fluid. The operation of two identical, back-to-back coupled syringe pumps 2 connected to each end of the cell allowed a steady flow of the system under study, with a pressure fluctuation smaller than 1.5 kPa. By

means of the six-way valve 3 a calibrated loop 4 (volume $0.634 \pm 0.002 \text{ cm}^3$) was connected either to the fluid stream or to a sampling system 5. The sampling system consisted of a high-pressure weighing bottle with a volume of 2.65 cm^3 and a cold trap, both connected to a vacuum pump. Finally, a carbon dioxide reservoir 6 was used to load the cell and the pump with this fluid, a positive displacement pump 7 delivers liquid solvent to the apparatus, either CO_2 or methanol, the latter to rinse the loop.

The cell, loop and pumps were maintained at constant temperature, within 0.03 K, by means of a thermostat water bath. The temperature of the system was assumed to be the same as the one measured in the bath, using a long-stem platinum thermometer with an accuracy of 0.1 K and a precision of 0.002 K. A pressure transducer (Druck PDCR 921), calibrated with a dead weight balance (Ruska) and thermostated at 313 K, allowed the measurement of the pressure in the carbon dioxide–azulene mixtures with an uncertainty of 0.01% and a precision of 0.1 kPa. The equilibration and sampling procedures were as follows. A solution of azulene in carbon dioxide was introduced into the cell from an auxiliary bottle where it had been prepared previously. Pure carbon dioxide was loaded into cell 1 from pump 7 until approximately equal volumes of vapor and liquid phases were present in the cell. The system was then stirred with a stainless steel encased magnetic bar for about 30 minutes until the pressure was constant, i.e., when the pressure attained the saturation equilibrium value. Since the saturation pressure of the azulene solution was 1 to 2 kPa lower than the vapor pressure of pure carbon dioxide at the same temperature, it was possible to load the sampling system and the upper syringe pump with pure carbon dioxide vapor at a pressure equal to the solution's saturation pressure. This was essential in order to avoid condensation inside the loop while sampling the vapor phase. The motor driving the two coupled syringe pumps was started at this moment at a flow rate of about $0.1 \text{ cm}^3/\text{min}$ and the sampling loop 4 was then incorporated into the fluid stream. After rinsing the loop with about 90% of the phase that was being sampled, the sample remaining in the loop was isolated and its contents were transferred into the sampling system. Carbon dioxide in the sampling system was vaporized and then condensed inside a high pressure weighing bottle cooled down to 77 K. During sample depressurization, the solute precipitated mostly inside the loop and the tubing, and a small fraction (below 0.2%) was retained in a trap maintained at 183 K. A mercury manometer allowed monitoring the pressure in the sampling system during this operation; it was kept always below 3 kPa. After this, liquid methanol (Merck CG) was flushed through loop and tubing by means of pump 7 in order to solubilize the precipitated azulene, and the methanol solution was collected in a weighted flask. The carbon dioxide contained in the bottle was weighed to within 0.0002 g and the amount of azulene in the methanol solutions was determined spectrophotometrically. Measuring the optical absorption of several solutions of azulene in methanol of known concentrations, we calculated for the molar absorptivity of these solutions the value $5407.1 \text{ m}^2 \text{ mol}^{-1}$ at 274.5 nm and 298.15 K. From the absorbance and the mass of the solutions the

TABLE I. Distribution of azulene between the coexisting liquid and vapor phases of CO₂.

T K	p MPa	ρ^L mol dm ⁻³	x	y	K_D
278.17±0.01	3.955±0.02	20.37	1.30×10 ⁻³	3.66×10 ⁻⁶	(2.82±0.24)×10 ⁻³
284.44±0.005	4.632±0.02	19.35	1.12×10 ⁻³	6.69×10 ⁻⁶	(5.98±0.45)×10 ⁻³
289.13±0.01	5.197±0.02	18.47	6.78×10 ⁻⁴	7.29×10 ⁻⁶	(1.08±0.07)×10 ⁻²
292.02±0.01	5.564±0.02	17.84	5.05×10 ⁻³	8.02×10 ⁻⁵	(1.59±0.06)×10 ⁻²
294.59±0.01	5.912±0.02	17.21	1.25×10 ⁻³	2.95×10 ⁻⁵	(2.35±0.09)×10 ⁻²
296.82±0.02	6.224±0.03	16.58	1.48×10 ⁻³	5.14×10 ⁻⁵	(3.46±0.13)×10 ⁻²
298.65±0.01	6.494±0.03	15.97	5.29×10 ⁻⁴	2.6×10 ⁻⁵	(4.91±0.22)×10 ⁻²
301.08±0.005	6.868±0.02	14.95	4.95×10 ⁻⁴	4.04×10 ⁻⁵	(8.15±0.31)×10 ⁻²
302.59±0.01	7.103±0.03	14.03	3.48×10 ⁻⁴	5.48×10 ⁻⁵	(0.158±0.006)
303.48±0.005	7.250±0.02	13.14	2.81×10 ⁻⁴	1.18×10 ⁻⁴	(0.250±0.020)
303.80±0.03	7.310±0.02	12.59	3.27×10 ⁻⁴	8.94×10 ⁻⁵	(0.289±0.066)

total mass of azulene could be calculated. Finally using the masses of carbon dioxide and azulene contained in the loop, the mole fraction of azulene in the carbon dioxide vapor phase solution and the density of the vapor phase could be calculated. Analysis of the liquid phase was accomplished in a similar manner.

Carbon dioxide (Coleman grade 4.0) and azulene p.a. (Aldrich 99%) were used in all the experiments without further purification. The equation of state of CO₂ proposed by Ely and co-workers was used.^{21,22} They employed the value of $T_c = 304.13$ K determined by Moldover.²³ The other critical constants for CO₂ are $p_c = 7.375$ MPa and $\rho_c = 10.63$ mol dm⁻³. The equation of state for CO₂ proposed by Span and Wagner more recently²⁴ gives densities for the saturated liquid differing less than 0.05% from those calculated with the equation of state in Ref. 21, which is the one we have used in this study.

IV. RESULTS

In this work we have determined the concentration of azulene in the coexisting vapor and liquid phases of CO₂ at 11 state points in the near-critical region. The experimental determination of the solute's concentration in each state required three days to be completed, starting with the preparation of the mixture and finishing with the determination of the composition of each phase. The first day involved loading the system and thermal equilibration of the apparatus; on the second day the appropriate volumes of the two phases were chosen and after ensuring proper equilibration the two phases were sampled very slowly to avoid undue perturbations in the system. On the third day the amount of solute in each phase was determined by measuring the UV optical density of the solutions prepared when the sampling loop was flushed with methanol.

In order to sample coexisting fluid phases in systems under near-critical conditions, special care must be taken because it is very hard to maintain homogeneity in each of the coexisting phases. Density fluctuations are easily induced by small temperature and/or pressure gradients, always present in flowing systems; these result in some mixing of the phases throughout the experimental apparatus. Our apparatus was designed to minimize pressure or temperature gradients during sampling, but this required a preliminary lengthy study to

set the optimal conditions of operation to guarantee that a portion of the equilibrated vapor or liquid phases in the flowing two-phase system could be isolated inside the loop without unduly perturbing phase equilibrium. As a test of reliable operation of the apparatus the densities of coexisting phases of pure carbon dioxide were measured and compared with those given by the equation of state of Ely *et al.*²¹ for the pure fluid.

For the binary system, the concentration of azulene in the two fluid phases was small, its mole fraction in the vapor phase was between 3×10^{-6} and 10^{-4} , and in the CO₂ liquid phase between 3×10^{-4} and 5×10^{-3} . As mentioned in Sec. III, the sampling method allowed the determination of the amount of substance for the two components in the two coexisting phases and from them we could calculate the densities of the two phases, this allowed us a further test of the experimental procedure. Using for the pure solvent the equation of state of Ely *et al.*,²¹ we calculated for each (p, T) point the density that pure CO₂ would have in the same thermodynamic state under vapor-liquid equilibrium conditions. From this calculation we establish that the concentration of azulene in the fluid was low enough so that its presence did not contribute significantly to the density of the fluid which, then, was equal to that of pure CO₂ at the same (p, T) .

For the vapor phase the square root of the quadratic standard deviation, σ^V , of the measured densities in the binary system from the values calculated with the equation of state of pure CO₂ for the 11 points was $\sigma^V = 0.10$ mol dm⁻³, with a maximum deviation of 4% at the lowest density, 2.60 mol dm⁻³, and 1% at the highest vapor density of 8.64 mol dm⁻³. For the liquid phase density, one experimental point was eliminated since it differed more than 2.5 standard deviations from the values calculated with the equation of state; the resulting σ^L was 0.19 mol dm⁻³, i.e., around 1% at all liquid densities. We think this verification was significant because it means that the true phase equilibrium conditions were attained and, hence, they tell about the precision of the measurements in the present study. Moreover, since good precision was obtained for the measured densities of pure carbon dioxide in the same temperature range, we conclude that the (p, ρ, T) behavior of the mixture does not differ appreciably from that of the pure solvent, hence the solute can be safely considered at infinite dilution.

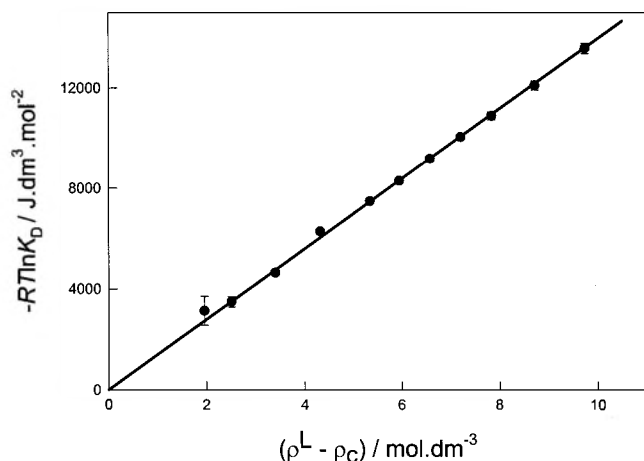


FIG. 2. $-RT \ln K_D$ against $(\rho^L - \rho_c)$ for azulene in carbon dioxide. ● experimental values, the bars give the error of each experimental point. K_D is the distribution ratio (y/x) at infinite dilution [cf. Eq. (5)].

Table I reports the experimental results, the liquid densities reported in column 3 are those calculated with the equation of state of Ely *et al.*²¹ for CO₂. The values of the mole fractions of azulene in the liquid phase were determined with an uncertainty smaller than 2%, while those in the vapor phase had an average uncertainty which was twice as large. Error propagation allowed us to estimate conservatively that 6% is the average uncertainty of the K_D values; the value at 303.80 K, which was only 0.33 K from T_{c1} , had a larger uncertainty as shown in Fig. 2.

V. DISCUSSION

In Fig. 2 the values of $-RT \ln K_D$ for azulene dissolved in carbon dioxide are plotted against $\delta\rho^L$ according to the asymptotic Eq. (8). The data were fitted with polynomials using equal weight for the data, under the condition that the fitting equation had to pass through the (0, 0) point. The best fit was obtained with a straight line, having a slope of 1397 J dm³ mol⁻², with a correlation factor of $r^2=0.99972$. Bars in the figure indicate the precision of the ordinates for each point calculated by propagation of the experimental uncertainties in the composition determinations, they are considered conservative estimates; the error bars are not bigger than the size of the symbols in the figure with the exception of the point closest to T_c which deviates from the straight line, although the deviation is within the experimental precision. The statistical analysis of the fit shows that the width of the 95% confidence range of the slope is within ± 16 J dm³ mol⁻² from the best value. Using the value we determined for the slope of the straight line in Fig. 2, the value of $J^c = -79.1 \pm 0.4$ MPa was obtained using the expression for the slope given by Eq. (8).

Jeon *et al.* have recently reported²⁵ values of the partial molar volume at infinite dilution, V_2^∞ , of azulene dissolved in supercritical CO₂ at different temperatures and fluid densities using the supercritical fluid chromatographic method. From the values that they reported it was possible to calculate J at all solvent densities and for all the isotherms, its values at $\rho_1 = 10$ mol dm⁻³, close to ρ_c , are given in Table

TABLE II. Literature values of the Krichevskii function J , for azulene in supercritical CO₂ determined by chromatography at $\rho = 10$ mol dm⁻³ (Ref. 24).

T_{red}	1.007	1.02	1.056	1.072	1.066
$-J/\text{MPa}$	58.3	29.6	20.6	20.0	20.2

II. It may be seen that at $T_{\text{red}}=1.007$, the experimental isotherm which is closest to T_c , J is 26% less negative than J^c obtained from the slope of $RT \ln K_D$ against $\delta\rho^L$ in the present study. However, Jeon *et al.* warn that V_2^∞ values for this isotherm may only be considered “*gross approximations*” due to uncertainties in the fluid density near criticality. Table II shows that the values of J calculated with the chromatographic data have a strong temperature dependence until, at $T_{\text{red}}=1.05$, it reaches an almost constant value around -20 MPa, this value is four times less negative than the value of J^c found in the present work. The steep change of J with temperature found by Jeon *et al.* is contrary to evidences from other studies that clearly suggest J has a weak temperature dependence.^{17,18,26} For the solute CHI₃ dissolved in CO₂ Fernández *et al.*²⁶ found that $(\partial J/\partial T)_\rho = 0.22$ MPa/K over a wide range of temperature above and below T_c , with the exception of the isotherm having $T_{\text{red}}=1.004$ where J shows a moderate decrease. It is not clear, however, if this is an experimental artifact due to the difficulties of spectrophotometric measurements too close to the critical state.

It can be shown⁶ that the hydrostatic hypernetted charin (HHNC) theory²⁷ for inhomogeneous fluids using a spherical Lennard-Jones intermolecular potential is capable of describing correctly the most relevant structural and thermodynamic features of nonpolar and weakly polar near-critical binary systems. We have used that theory to calculate J for azulene in CO₂ at three fluid densities close to ρ_c using the Lennard-Jones parameters of the solute, $(\epsilon_2/k)=660$ K and $\sigma_2=0.66$ nm;⁶ the results are plotted against $\tau=1-T_{\text{red}}$ in Fig. 3. The values of J for $\rho_{\text{red}}=(\rho/\rho_c)=1.05$ are very close to the ones obtained in this work from $RT \ln K_D$ and Eq. (8). Moreover, Fig. 3 shows that the theory lends support to the frequently reported weak temperature dependence of J .

We have found that the best order parameter to represent the asymptotic behavior is $\delta\rho^L$, although $(\delta\rho^L - \delta\rho^V)$ performs also very well. This is not the case of δV^L as order parameter. This indicates that density is the natural variable to represent the asymptotic behavior. According to Eqs. (6) and (7), the fact that the linear behavior extends far from T_c may be deemed to occur because $\Psi_{\rho_2\rho_1}^{c,r} \delta T \ll \Psi_{\rho_2\rho}^{c,r}$. Actually an estimate of the value of the second term in Eq. (6), which is directly related to J_T^c , can be obtained from the study of the solubility of CHI₃ in CO₂, because this solute has Lennard-Jones parameters which are very similar to those of azulene.²⁶ If this assumption is correct, the second term in the expansion would contribute at most 7% to $RT \ln K_D$ at the lowest temperature. This is a small contribution, but should have been experimentally observed.

For the distribution equilibrium constant of heavy water between light water and steam a very short asymptotic region

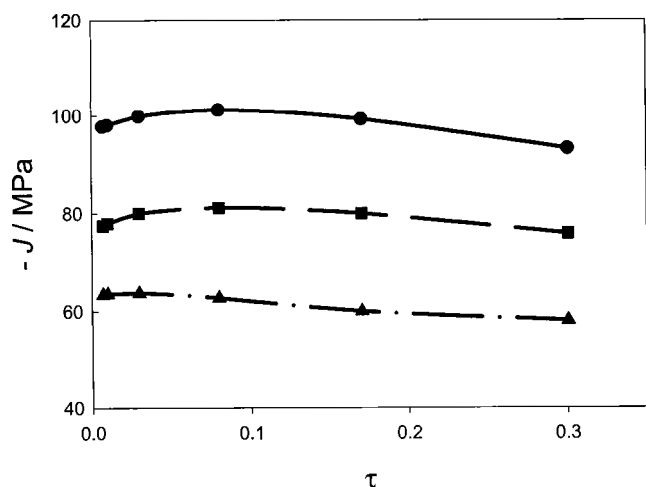


FIG. 3. $-J$ against τ for azulene in CO_2 calculated with the HHNC theory using a Lennard-Jones intermolecular potential with the molecular parameters given in the text. ●, $\rho_{\text{red}}=1.23$; ■, $\rho_{\text{red}}=1.05$; ▲, $\rho_{\text{red}}=0.88$. J is the Krichevskii function $(\partial p/\partial x)_{T,V}^{\infty}$.

has been observed.¹⁰ This feature was attributed to the almost ideal behavior of the mixture which implies that for the isotopomere mixture $\Psi_{\rho_2\rho}^{c,r}$ has a smaller magnitude than the second term in Eq. (6). This is not the case for other binary systems containing solutes which are not so similar to the solvent as D_2O and H_2O are. For these systems $\Psi_{\rho_2\rho T}^{c,r}\delta T$ is small compared to the first coefficient in the expansion, as already shown. The existence of a reduced linear-behavior region for mixtures of light and heavy water has been also shown by the theoretical study of Abdulkadirova *et al.*,²⁸ who made a detailed analysis which included crossover between the Ising and the classical critical regions.

It is clear that in order to account quantitatively for the extended range of the linear asymptotic behavior observed in the azulene- CO_2 near-critical system, it is necessary to use a complete theory which includes crossover. Hence the quantitative explanation of the extension of the linear range for $-RT \ln K_D$ against $\delta\rho^L$ observed in the present work offers a challenge which requires a thorough theoretical analysis.

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