



Near-critical and supercritical dilute solutions viewed from macroscopic and molecular-scale perspectives

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ABSTRACT

Partial molar properties of dilute solutes in near-critical solvents exhibit a strong dependence on temperature and density which hinders the description of their behaviour under those conditions. We used the well-behaved Krichevskii function, $J = (dp/dx)V, T$ supra infinity, to describe that region of the thermodynamic space, and have extended its use to ternary solutions (two solutes + one near-critical solvent) successfully. The use of supercritical solvents permits a controlled and continuous exploration of the density dependence of solutes' properties without undergoing phase transitions, hence the availability of a non-diverging property like J to describe the systems is greatly important. We show its application for binary and ternary systems that have been studied and also give some information about the molecular structure of near-critical solutions. This knowledge provides a better understanding about solvation and its dependence on long-range (critical) fluctuations in the presence of intermolecular interactions.

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1. Introduction

One hundred years ago J. van der Waals was awarded the Nobel Prize in Physics for deriving an equation of state (EoS) for the liquid and gaseous states of pure fluids which was the result of a clever, albeit simple, molecular model that recognized the effect of attractive and repulsive interactions among molecules [1]. Not only this EoS was very successful in dealing with the main features of fluid phase equilibria, including the metastable states according to the principle of continuity of states, it also contained the seed of the law of corresponding states of so wide application [2]. It was also able to describe the critical state between liquid and vapour phases; however, the details of the nonanalytical behaviour required to deal with the vicinity of the critical point has been ever since an obstacle for a quantitative description of the critical state. In spite of the mean-field nature of his EoS, van der Waals recognized that the region between liquid and vapour phases in equilibrium involved a strong inhomogeneity in the molecular density over very small distances, a view that has been of great importance in the present consideration of interfacial phenomena.

Great effort has been devoted since then to describe the near-critical region of fluids [3–6], and more recently also of solutions,

where the solvent medium is close to its critical state [7–11]. Improvement of the predictive capacity of van der Waals' type (cubic) EoS for fluids has shown that the basic foundations of the original van der Waals equation remain valid [2].

Supercritical solvents have been studied for the last 20 years due to their numerous applications to chemical, food, materials and pharmaceutical industries; these studies are to a large extent the mainstream of the work published in this *Journal*. In addition, supercritical solvents have also contributed importantly to our understanding of many phenomena related to solute–solvent molecular interactions, e.g. solvation, and the role played by interactions in reaction mechanisms [12]; they also provided a way to understand important dynamic aspects, like the transition from the energy-transfer regime, that characterises gaseous behaviour, to the friction-controlled regime exhibited by liquid solvents [13–15].

In a series of studies we have investigated the near-critical behaviour of solutions, including their thermodynamic properties as well as their molecular features. Two main topics, characteristic of solutions in near-critical or supercritical solvents, captured most of our interest:

- The singular thermodynamic or macroscopic behaviour of the system due to the proximity of a critical point.
- The structural changes induced by solvation as the solvent's density is continuously varied, i.e. the exploration of the molecular consequences of the “continuity of the gas and liquid states” envisaged by van der Waals.

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In this work we give an overview of these two topics, highlighting the importance of a non-divergent property, the Krichevskii function, determined by solute–solvent interactions and capable of dealing with the behaviour of binary and ternary systems in the near-critical regions of fluid phase equilibria.

2. Asymptotic behaviour of dilute solutions near the solvent's critical point

As a consequence of the proximity of binodal and spinodal curves in near-critical fluids, experiments need careful planning because some response functions approach zero, hence the system's ability to respond to external perturbations or to internal non-equilibrium configurations is strongly reduced [10].

One of the most difficult aspects encountered in the experimental study of fluid systems close to a critical point (CP) is that small temperature or pressure gradients in the cells, presumed at equilibrium, have an unusually strong effect on the density; consequently experimental conditions should be carefully established [16,17] as real behaviour in the near critical region may be masked by experimental flaws [18,19]. In addition, several solute's properties frequently used to describe the behaviour of dilute solutions near the solvent's triple point diverge or become zero at the solvent's CP, and their effect is perceived over a wide region around it.

Moreover, fluctuations play a paramount role in the behaviour of near-critical fluids. Since classical EoSs, like that of van der Waals, do not take into account density or energy fluctuations, they are not able to describe the correct behaviour of fluids in the vicinity of the critical point, and non-classical equations are required. The strategy we adopted to circumvent this serious impediment in the description of dilute solutions in near-critical solvents was to represent the diverging properties (e.g. the solute's partial molar volume, isobaric partial molar heat capacity and partial molar entropy) by a product between the near-critical properties of the pure solvent and a quantity that accounts for solvent–solute interactions: the Krichevskii function $J = (\partial p / \partial x)_{V,T}^\infty$. For instance, the following equations give the partial molar volume and entropy of the solute at infinite dilution using J and properties of the pure solvent: its compressibility and expansion coefficients.

$$V_2^\infty = V_1^* + V_1^* \kappa_T^* J \quad S_2^\infty = S_1^* + V_1^* \alpha_p^* J \quad (1)$$

The advantage of this approach is that, for dilute solutions over a wide p – T range around the solvent's CP, the well-behaved Krichevskii function J shows no evidence of a singular critical contribution. J depends mainly on the solvent's density, temperature playing a less important role. As an example, the values of J obtained from partial molar volumes for aqueous solutions of CO_2 and NaCl are illustrated in Fig. 1a and b, respectively [20,21]. Both figures depict the strong change in the solute's partial molar volumes V_2^∞ as the near-critical region is approached: positive values for volatile solutes like CO_2 , negative for non-volatile solutes like NaCl . In contrast to the singular behaviour of V_2^∞ , J does not show any indication of anomalies near the critical state.

Classical expansions [8,9] show that the value of J at the solvent's critical point (J^c , called the Krichevskii parameter) determines not only the amplitude and sign of the divergence of the solute's partial molar properties but also the solute's concentration corresponding to phase equilibria conditions in the vicinity of the solvent's CP. Two important asymptotic relations derived by Japas and Levelt Sengers [22] have been employed to describe the solubility of gases in liquids up to the solvent's critical point as a function of the solvent's density in terms of the Krichevskii parameter J^c . Thus, expressions

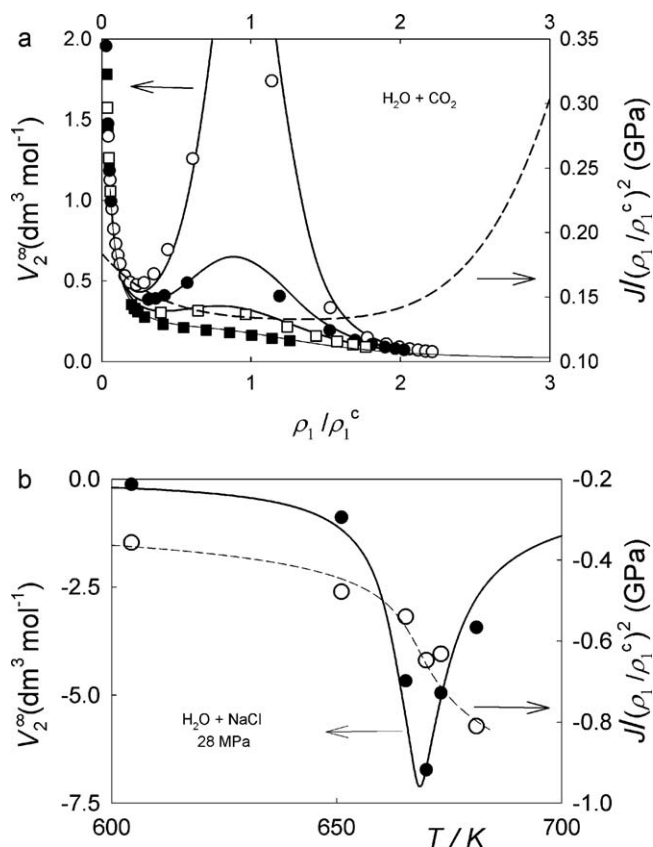


Fig. 1. Partial molar volume at infinite dilution (left axis) and reduced Krichevskii function $J/(\rho_1/\rho_1^c)^2$ (right axis) of CO_2 (upper panel) and NaCl (lower panel) dissolved in water. For $\text{CO}_2 + \text{H}_2\text{O}$, the data are plotted as a function of the reduced density ρ_1/ρ_1^c . V_2^∞ were taken from Gallagher et al. [20] for 660 K (open circles), 700 K (full circles), 750 K (open squares) and 850 K (full squares) while solid lines represent calculated values for each temperature using Eq. (1), pure water properties and a constant mean value of $J/(\rho_1/\rho_1^c)^2$. The dashed line depicts the density dependence of $J/(\rho_1/\rho_1^c)^2$ for $\rho_1/\rho_1^c < 2$. For $\text{NaCl} + \text{H}_2\text{O}$ (lower panel) the full symbols represent the values of V_2^∞ measured by Majer et al. [21] as a function of T along the 28 MPa isobar while the solid line depicts the calculated values using Eq. (1), pure water properties and the mean value of $J/(\rho_1/\rho_1^c)^2$. Open circles represent the values of $J/(\rho_1/\rho_1^c)^2$ calculated for each data point and the dashed line is a guide to the eyes for $J/(\rho_1/\rho_1^c)^2$.

for the asymptotic behaviour of Henry's constants ($T \ln(k_H/f_1^*)$), where f_1^* is the solvent's fugacity, and the distribution equilibrium constant ($T \ln K_{\text{dist}}$) of the solute between the liquid and the vapour phases are now available. These expressions provide the exact limiting behaviour in the vicinity of the CP and, combined with classic well-behaved equations that describe liquids near the triple point, allow calculating the values for the thermodynamic properties of solutions right to the solvent's CP with good precision. Their use was of paramount importance for the description of the solubility of nonreactive gases in water over the complete region of coexistence of liquid–vapour equilibrium, as shown by Fernández-Prini et al. [23]. Moreover, it was shown that this description can also be extended to pressures about 50 MPa above the solvent's vapour pressure [24].

From K_{dist} data, the values of J^c for many aqueous solutions have been determined [25]. It has been shown that the values of J^c for water containing non-polar volatile solutes, from He to C_8H_{18} , present very similar values of J^c , around 0.17 ± 0.01 GPa, despite having very different interaction parameters and very different binary solute–water critical lines. The remarkable constancy of J^c for these solutes is qualitatively explained by the van der Waals EoS

which gives:

$$\frac{J}{\rho_1^2} = 2RT \frac{(b_{12} - b_{11})}{(1 - \rho_1 b_{11})^2} - 2(a_{12} - a_{11}) \quad (2)$$

For SF₆, a weakly interacting but larger solute, J^c increases to 0.21 GPa. On the other hand, solutes having more attractive interactions (n - π , dipolar and H-bonding) with water have lower values of J^c , e.g. 0.044 GPa for NH₃ and 0.038 GPa for ethanol [25]. Attractive¹ solutes have negative values of J^c , as shown in Fig. 1b, because they interact strongly ($a_{12} > a_{11}$) with the solvent.

Following the advances in the study of the critical vicinity of binary dilute solutions [26], we advocate the use of Krichevskii function, an EoS in Callen's description [27], as a very convenient quantity to describe the thermodynamic behaviour of dilute solutions in near-critical solvents, since it does not have critical singularities. Moreover, as predicted by the van der Waals EoS, Eq. (2), at low and intermediate densities the values of J/ρ_1^2 should be only a weak function of temperature and density. For the H₂O + CO₂ system, where information of V_2^∞ is available over a wide temperature range (440–1000 K), the J/ρ_{red}^2 data ($\rho_{\text{red}} = \rho_1/\rho_1^c$) of all isotherms collapse into a single curve. Regarding the density dependence, Fig. 1a shows for a repulsive solute that the values of J/ρ_{red}^2 remain almost constant for all densities up to twice the critical density, while at higher densities, the contribution of the repulsive term becomes relevant; a similar conclusion can be drawn for attractive solutes (Fig. 1b). This behaviour supports our contention about the utility of the J function to describe the behaviour of near-critical solutions: the curves for V_2^∞ shown in each panel of Fig. 1 were calculated using a constant mean value of J/ρ_{red}^2 (0.15 GPa for CO₂ and –0.62 GPa for NaCl), i.e. independent of temperature and density.

This thermodynamic treatment has also been extended recently to ternary systems and their description has been applied to study the effect of co-solutes on the solubility of solids near the critical solution endpoint [28]. In the vicinity of the binary critical endpoint, the solubility of solids in supercritical solvents shows strong variations with pressure or temperature, as a consequence of the diverging osmotic susceptibility of the binary system [10]. The addition of a third component (co- or anti-solvent) at constant pressure and temperature, has also a great impact on near-critical solubilities; for liquids near the triple point this effect is described in terms of the Setchenov's constant K_S , which can adopt positive (salting out) or negative (salting in) values, depending on the interactions between solute, cosolute and solvent. At the critical end-point of the (solute + solvent) binary system, K_S diverges similarly to V_2^∞ in a binary mixture at the solvent's critical point, i.e. both properties are isomorphic. K_S is proportional to the osmotic susceptibility of the binary solute–solvent system, or, to the pressure dependence of the solubility in the binary solvent–solute system, as given by Eq. (3), where symbol σ indicates the coexistence (solid + fluid) line and refers to the binary system, i.e. without cosolvent.

$$K_S = \frac{1}{x_2^{\sigma,\circ}} \left(\frac{dx_2}{dp} \right)_{T,\sigma}^\circ J_{K3}^\sigma \quad (3)$$

The scale factor J_{K3}^σ , which determines the sign and amplitude of the divergence of K_S , is related to the initial slopes of the critical end-line of the ternary system. Nonvolatile co-solvents ($J_{K3}^\sigma < 0$) increase the solubility of solids ($K_S < 0$). As an example, the effect of NaCl on the solubility of quartz in near critical water is illustrated in Fig. 2. Symbols depict experimental data [29–31], covering the temperature range 638–703 K and NaCl molalities up to 4 mol, while the curves show predicted values, calculated with Eq. (3) using

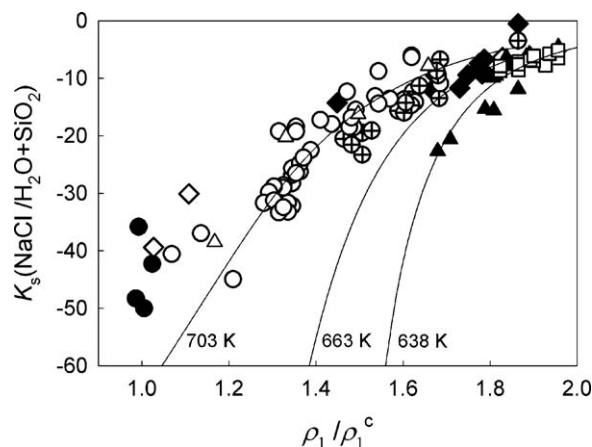


Fig. 2. Setchenov constant, $K_S = (d \ln x_{\text{SiO}_2} / dx_{\text{NaCl}})_{T,p,\sigma}$, measuring the effect of the addition of NaCl on the solubility of SiO₂ in H₂O. Experimental data are taken from: Foustoukos and Seyfried [29] at 638 K (full diamonds), 648 K (crossed circles), 663 K (open circles), 693 K (open diamonds) and 703 K (full circles); Von Damm et al. [30] at 636 K (full triangles) and 673 K (open triangles); Fournier et al. [31] at 623 K (open squares). Lines at three temperatures were calculated using Eq. (3), with the pressure dependence of the SiO₂ solubility as given by Von Damm et al. [30], the approximation $J_{K3}^\sigma \approx J_{\text{NaCl}}^\sigma$, the Krichevskii parameter of the (H₂O + NaCl) binary system.

only information from the binary systems: $(d \ln x_2 / dp)_{T,\sigma}$ from the binary (H₂O + SiO₂) and J^c from the binary (H₂O + NaCl), as the small solubility of SiO₂ in H₂O allows replacing J_{K3}^σ of the ternary H₂O + SiO₂ + NaCl system by J^c of the binary (H₂O + NaCl), see [28].

3. Effect of the coupling of long-range solvent fluctuations with short-range intermolecular interactions

The fact that solutes' partial molar properties present a very strong change when temperature increases towards the solvent's CP was interpreted some 20 years ago in terms of the formation of an extremely large cluster of solvent molecules around attractive solutes and the depletion of solvent molecules around repulsive solutes [32,33]. As shown in the previous Section, we now know that such extreme solvation hypothesis was incorrect, the observed changes in the solutes' properties are due to the interplay of long-range critical fluctuations with short-range interactions. However, this was an incentive to study near-critical solutions in order to assess the effect of the CP upon solvation.

It has been claimed that the study of isolated clusters formed by one attractive solute particle, ionic [34] as well as molecular [35] species, surrounded by an increasing number of solvent molecules, is a very convenient strategy to assess the gradual building up of the solvation structure in solution, a perspective that would bridge the molecular and macroscopic domains. In the last years, small and medium size molecular clusters have been investigated in detail, giving a comprehensive insight into the structure and the dynamic processes associated principally to the first solvation shell. In most cases the results emerging from these studies cannot be completely rationalised in terms of the properties of bulk solutions, mainly because thermodynamic variables, as temperature and pressure, are not well defined in confined (subnanometer) systems and the influence of solvent–solvent forces beyond the first solvation shell cannot be accounted for. For instance, within the size range covered in solvation studies of clusters most of the solvent molecules are at the cluster's surface, hence their structure will not be a representative sample of the local environment around the solute in a solution. Surface discontinuity necessarily perturbs the orientation of the molecules with respect to the structure adopted in the bulk, thus limiting greatly the use of clusters in order to study the first solvation shell of dissolved solutes.

¹ Meaning that the solute–solvent interaction is larger than the solvent–solvent one.

The special features that characterise the behaviour of dilute supercritical solutions, mainly those containing highly attractive solutes, make these fluid media good candidates for performing solvation studies by changing continuously the solvent's density without the appearance of phase transitions. As a first approach to describe the solvation environment, we have analysed the behaviour of some partial molar quantities in near-critical solvents which were determined for different systems on the basis of solubility measurements and its changes with pressure and temperature. For example, we have found evidence that the solubility of solutes, either nonpolar (I_2) or slightly polar (CHI_3), in various non-polar supercritical solvents and also in CHF_3 cannot be described in terms of multipole interactions and isotropic dispersion forces [36]. Their description requires a finer consideration of the structure of the solute (down to the charge distribution at an atomic level) [37]. This type of study has underlined the effect on solvation of the atomic groups in the solute molecules which becomes more dominant in an expanded solvent [38]: thus solvent molecules interact preferentially with those regions of the solute molecule having an adequate local charge distribution, and the interplay of solvent-probe *vis-à-vis* solvent-solvent interactions results of great importance.

At higher densities, a compact and rather stable moiety rapidly develops around the solute, usually containing a small number of solvent molecules in the first solvation shell. At this point, the typical local density within the moiety might be comparable to that found in condensed phases or clusters, showing an abrupt decrease of solvent molecules at longer distances from the solute. According to the relative magnitude of solute-solvent and solvent-solvent forces, this change of density will depend on the interaction between the solvent molecules in the first solvation shell with those in the second solvation shell; this interaction will be enhanced as the density increases.

Solvatochromic solutes, i.e. molecules whose ground and excited state energies change differently upon solvation, have been often employed as probes in near-critical solvents to observe structural changes occurring mostly in the solute's first solvation shell (i.e. "direct" solvation effects dominate the spectral shift). The effect of solvent's density on intermolecular solute-cosolvent charge transfer bands allows the study of preferential solvation phenomena. For example, it was possible to show that the charge transfer between iodine and arene molecules dissolved in supercritical nonpolar solvents requires a detailed description of the solute-solvent collisions that produce the charge transfer process [39].

In the last years [40] we explored another type of photochemical probes that exhibit a higher susceptibility to the density and temperature changes occurring in the fluid. These are photoactive species which undergo charge transfer to solvent (CTTS) states and can be generated, for instance, by UV absorption of a solvated halide anion or alkali halide contact ion pair (CIP). The position of the CTTS absorption band of both photoactive species can be monitored as a function of the solvent density. In Fig. 3 we show the absorption spectra of KI in supercritical NH_3 (SCA) measured at 420 K and two different reduced densities. The overall band was separated in two Gaussian components which correspond to the free iodide ion (a) and CIP (b) CTTS absorptions. From the UV-VIS spectra of KI in SCA recorded as function of fluid density at $T = 420$ K it was possible to establish that separated pairs or free iodide ions prevailed at high densities, as expected, while CIPs dominated when the density is lower.

Making use of calculations at different solvent densities we found that similarly to iodide ions, photoexcitation of KI CIPs changed from an intramolecular electron transfer, in the isolated molecule and low density solutions, to a CTTS excitation when the reduced density is above 0.2. At the bottom of Fig. 3 we illustrate

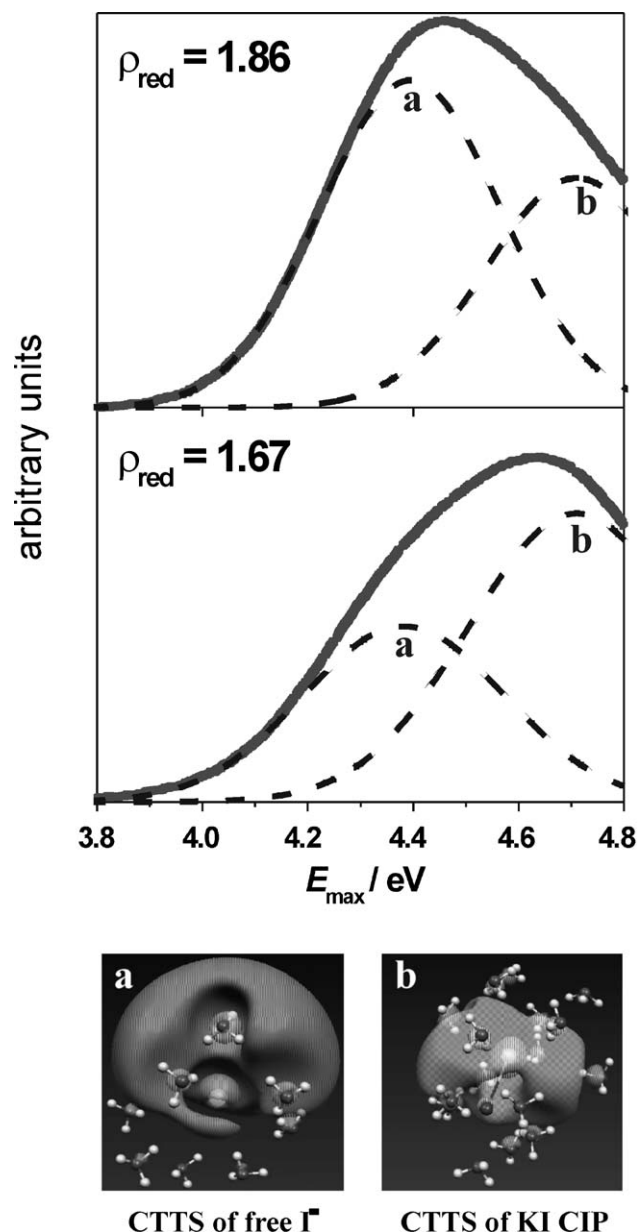


Fig. 3. Effect of $\rho_{red} = \rho_1 / \rho_1^c$ upon the UV-absorption of KI in SCA. In the upper panel the amount of free iodide ion is larger than in the lower panel, where the KI CIP predominates. At the bottom of the figure the spatial distribution of solvent molecules and the CTTS electron are shown for both species.

the representative solute's environment of each component of the band (KI CIP and I^-) in the CTTS excited state, obtained by quantum calculations subsequent to a molecular dynamics sampling [37]. KI CIP and the iodide ion, as well as the NH_3 molecules, are represented as balls and sticks, while the spatial distribution of the CTTS electron is depicted by isodensity contours. The remarkable susceptibility of these species to changes in the solvent density is due to their highly diffuse electronic excited states, with a considerable extent of electronic charge distributed among the voids formed in the solvent structure.

As an example of the importance for the physical chemistry of solvation, only by using SCA it was possible to verify that the previously reported effect of temperature changes upon the CTTS band of iodide ion, observed under liquid-vapour equilibrium conditions for liquid solvents, is really due to the changes in the fluid's density, as suggested (although never proved) before [41]. Thus, it has

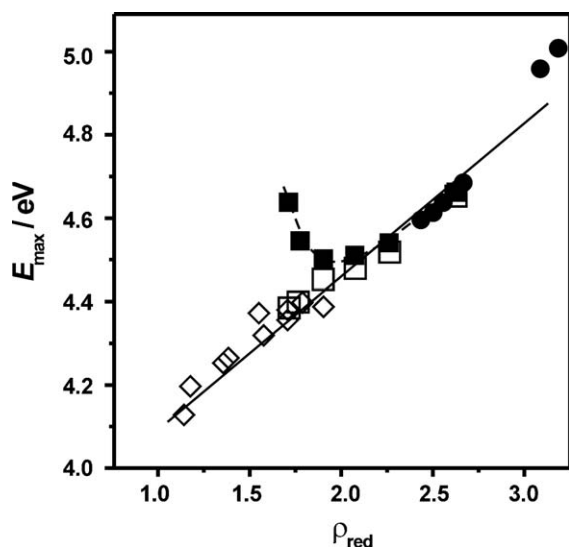


Fig. 4. Energy of the maximum in the absorption band of KI dissolved in ammonia. ●, measurements in liquid NH_3 in equilibrium with its vapour [40,41]; ■, our measurements at higher temperatures for the overall maximum; □, same data but only including the maximum of the band component corresponding to iodide ion; ◇, our data for iodide ion in SCA.

been possible to show that the energy of the CTTS peak (E_{max}) for free iodide in ammonia is linear in fluid density over a large region including gas-like and liquid-like densities. In Fig. 4, we plotted the energies of the overall (free I^- and CIP) absorption's maximum of KI dissolved in liquid ammonia [42,43] (●) which appear to be well

aligned with our E_{max} measurements corresponding to the iodide component of the band, in liquid at high temperature (□), but also in supercritical (◇) NH_3 . Note that the overall band maxima data in liquid ammonia at high temperature (■) show a reversal in the temperature effect that disappears after discounting the contribution of the CIP (□).

These results confirmed beyond reasonable doubt that fluid density is the most important thermodynamic variable that determines the energy of excitation of iodide ion in solution.

One interesting observation derived from our study of the particular thermodynamic states of dilute solutions in supercritical solvents is that CIPs, of alkali metal halides, are more soluble in SCA than in supercritical water (SCW). The simulation experiments [44] show that in water the H_2O – H_2O interaction, being particularly strong, competes with the solvation of the dipolar CIP much more than in ammonia. On the other hand, in SCA a persistent moiety formed by 4 NH_3 molecules is strongly attached to the KI CIP, remaining almost intact along the simulations; such a stable solvation structure is not visualized in SCW, where the number of first neighbours is reduced to two molecules and their orientations are found to be strongly influenced by the rest of the water molecules.

The important differences found in the solvation structure of KI CIPs dissolved in SCA or SCW, especially the one related to the interaction of first solvation shell with the bulk solvent, leave a clear signature in the energy diagram associated to the CTTS (E_{max}) and vertical electron detachment (VDE*) transitions (as shown in Fig. 5) where the calculation was done considering only the first solvation shell (dashed lines) or when the entire system was included (full lines) [44,45]. The difference between both calculations was attributed to the long-range solvation effect, this has little influ-

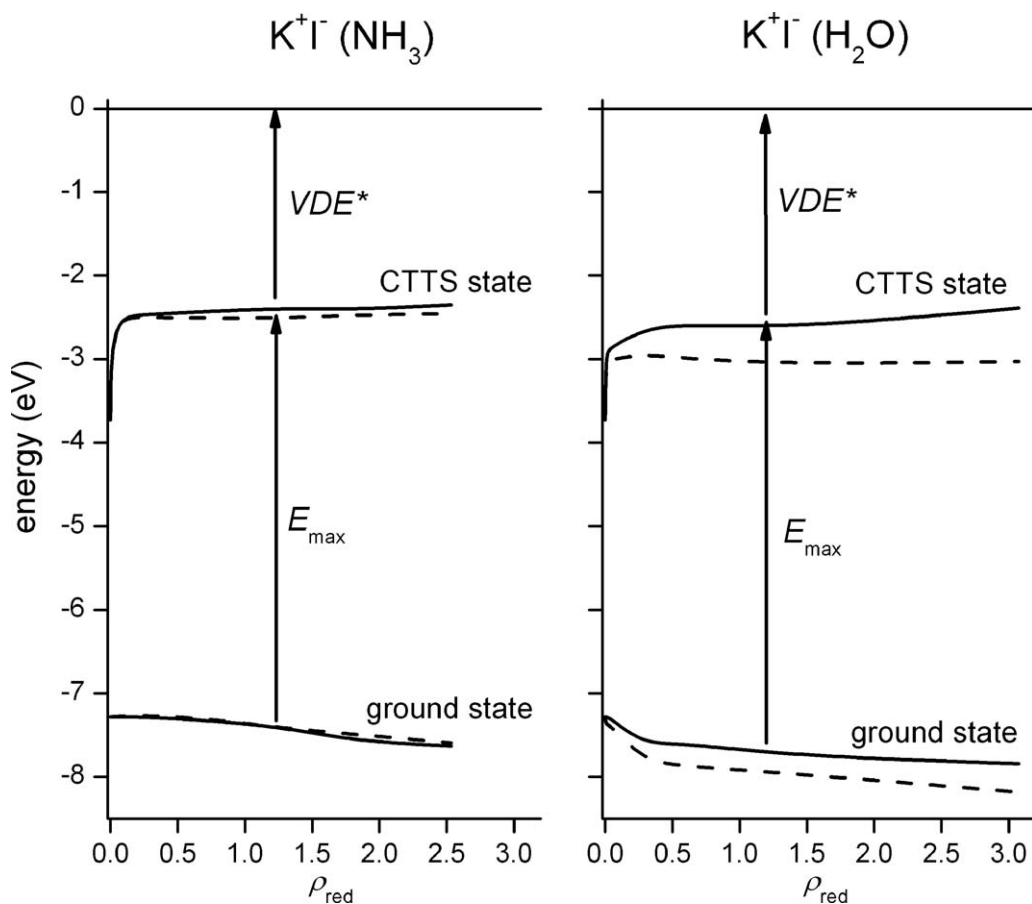


Fig. 5. Ground and CTTS excited state energies of the CIP of KI as a function of the reduced density. Left panel: SCA; right panel: SCW. E_{max} : CTTS transition; VDE*: vertical electron detachment. Solid curves: calculations for the complete solvent simulation box; dashed curves: only the first neighbour solvent molecules.

ence when the solvent is NH_3 but it destabilises the ground and CTS states in H_2O : the different behaviour can be attributed to the effect of the stronger solvent–solvent interaction in SCW than in SCA.

4. Concluding remarks

The Physical Chemistry of solutions has benefited from the use of supercritical solvents by providing a means to describe the properties of solutes up to the solvent's CP using, for instance, the Krichevskii function and asymptotic relationships. Moreover, the consequence of coupling the long-range correlation of solvent molecules close to the solvent's critical point with the short range intermolecular interactions between the solvent and an attractive solute has been clarified. Several authors, including our group, have suggested the existence of molecular inhomogeneities in the solvent's environment close to an attractive solute. The linear response theory indicates [46,47] that when these two effects are coupled the solvent's molecular density will increase close to the solute particles due to the influence of the large susceptibility of the fluid on the intermolecular interactions. We have now observed an analogous change in the composition of binary solvents close to an attractive solute.

It can be seen that the main advantage of using supercritical solvents (SCS) is that intermolecular interactions, including the effect of particular groups in the solute, or the consequence of strong solvent–solvent interactions, can be tuned by modest changes in the pressure or chemical potential, providing an unique way to study, at a microscopic level, the effect of interactions on macroscopic properties. For solute's partial molar properties, this information is captured by the Krichevskii function J , a non-divergent property that is essentially determined by the solvent's density. The possibility provided by SCS of studying in an uncoupled way the effects of temperature and density has allowed us to establish the small effect temperature has on J , a crucial observation in order to understand why asymptotic relations for Henry's and distribution constants were applicable far from critical conditions. The uncoupling of temperature and density has also helped in understanding phenomena like the charge transfer.

The availability of a non-divergent property like J , which is able to describe the near-critical systems, is relevant to establish the most convenient temperature and pressure for applying a given process. Moreover, SCS form a single solvent fluid phase, thus precluding the presence of interfacial phenomena. On the other hand, the possibility that the critical inhomogeneities can favour some chemical processes, remains a speculation with no practical consequences so far.

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References

- [1] J.-L. Barrat, J.-P. Hasen, *Basic Concepts for Simple and Complex Liquids*, Cambridge University Press, Cambridge, UK, 2003.
- [2] A. Kostrowicka Wyczalkowska, J.V. Sengers, M.A. Anisimov, *Critical fluctuations and the equation of state of Van der Waals*, *Physica A: Statistical Mechanics and its Applications* 334 (2004) 482–512.
- [3] B. Widom, *Equation of state in neighborhood of critical point*, *J. Chemical Physics* 43 (1965) 3898–3905.
- [4] K.G. Wilson, *Renormalization group and critical phenomena. I. Renormalization group and the Kadanoff Scaling Picture*, *Physical Review B* 4 (1971) 3174–3183.
- [5] M.E. Fisher, *The theory of equilibrium critical phenomena*, *Reports on Progress in Physics* 30 (1967) 615–730;
- [6] M.E. Fisher, *The theory of equilibrium critical phenomena*, *Reports on Progress in Physics* 31 (1968) 418;
- [7] M.E. Fisher, *Renormalization group in theory of critical behavior*, *Reviews of Modern Physics* 46 (1974) 597–616.
- [8] J.V. Sengers, J.M.H. Levelt Sengers, *Thermodynamic behavior of fluids near the critical point*, *Annual Review Physical Chemistry* 37 (1986) 189–222.
- [9] R.B. Griffiths, J.C. Wheeler, *Critical points in multicomponent systems*, *Physical Review A* 2 (1970) 1047–1064.
- [10] I.R. Krichevskii, *Thermodynamic of critical phenomena in infinitely dilute binary solutions*, *Russian, J. Physical Chemistry* 41 (1967) 1332–1338.
- [11] A.M. Rozen, *The unusual properties of solutions in the vicinity of the critical point of the solvent*, *Russian, J. Physical Chemistry* 50 (1976) 837–845.
- [12] J.M.H. Levelt Sengers, *Thermodynamics of solutions near the solvent's critical point*, in: T.J. Bruno, J.F. Ely (Eds.), *Supercritical Fluid Technology*, *Reviews in Modern Theory and Applications*, CRC Press, Boca Raton, FL, 1991, pp. 1–56.
- [13] M.L. Japas, R. Fernández-Prini, *Chemistry in near-critical fluids*, *Chemical Society Reviews* 23 (1994) 155–163.
- [14] R.E. Westacott, K.P. Johnston, P.J. Rossky, *Stability of ionic and radical molecular dissociation pathways for reaction in supercritical water*, *J. Physical Chemistry B* 105 (2001) 6611–6619.
- [15] M. Lee, G.R. Holtom, M. Robin, Hochstrasser, *Observation of the kramers turnover region in the isomerism of trans-stilbene in fluid ethane*, *Chemical Physics Letters* 118 (1985) 359–363.
- [16] D. Schwarzer, J. Troe, M. Votsmeier, M. Zerezke, *Collisional deactivation of vibrationally highly excited azulene in compressed liquids and supercritical fluids*, *J. Chemical Physics* 105 (1996) 3121–3131;
- [17] D. Schwarzer, J. Troe, M. Zerezke, *The role of local density in the collisional deactivation of vibrationally highly excited azulene in supercritical fluids*, *J. Chemical Physics* 107 (1997) 8380–8390.
- [18] P.A. Hoijemberg, J. Zerbs, M.L. Japas, C.A. Chesta, J. Schroeder, P.F. Aramendia, *Cage effect in supercritical fluids and compressed gases in the photolysis of an asymmetrically substituted diazene*, *J. Physical Chemistry A* 113 (2009) 5289–5295.
- [19] L. Bronstein, D.P. Fernández, R. Fernández-Prini, *Near-criticality in dilute binary mixtures: distribution of azulene between coexisting liquid and vapor carbon dioxide*, *J. Chemical Physics* 117 (2002) 220–225.
- [20] G. Sciaini, *Thesis, Universidad de Buenos Aires*, 2006.
- [21] R.S. Urdahl, D.J. Myers, K.D. Rector, P.H. Davis, B.J. Cherayil, M.D. Fayer, *Vibrational lifetimes and vibrational line positions in polyatomic supercritical fluids near the critical point*, *J. Chemical Physics* 107 (1997) 3747–3757;
- [22] D.J. Myers, M. Shigeiwa, M.D. Fayer, B.J. Cherayil, *Vibrational lifetimes and spectral shifts in supercritical fluids as a function of density: experiments and theory*, *J. Physical Chemistry B* 104 (2000) 2402–2414.
- [23] D.P. Fernández, G. Hefter, R. Fernández-Prini, *The solubility of solids in near-critical fluids. VI CH_3I in CO_2 revisited*, *J. Chemical Thermodynamics* 33 (2001) 1309–1324.
- [24] J.S. Gallagher, R. Crovetto, J.M.H. Levelt Sengers, *The thermodynamic behavior of the CO_2 – H_2O system from 400 to 1000 K, up to 100 MPa and 30% mole fraction of CO_2* , *J. Physical and Chemical Reference Data* 22 (1993) 431–513.
- [25] V. Majer, L. Hui, R. Crovetto, R.H. Wood, *Volumetric properties of aqueous 1–1 electrolyte solutions near and above the critical temperature of water I. Densities and apparent molar volumes of NaCl(aq) from 0.0025 mol kg^{-1} to 3.1 mol kg^{-1} , 604.4 K to 725.5 K, and 18.5 MPa to 38.0 MPa*, *J. Chemical Thermodynamics* 23 (1991) 213–229.
- [26] M.L. Japas, J.M.H. Levelt Sengers, *Gas solubility and Henry's law near the solvents critical point*, *AIChE J.* 35 (1989) 705–713.
- [27] R. Fernández-Prini, J. Alvarez, A. Harvey, *Henry's constants and vapor–liquid distribution constants for gaseous solutes in H_2O and D_2O at high temperatures*, *J. Physical and Chemical Reference Data* 32 (2003) 903–916.
- [28] J.L. Alvarez, R. Fernández-Prini, *A model-guided determination of $\Delta_{\text{dis}}G_2^\infty$ for slightly soluble gases in water using solubility data*, *J. Solution Chemistry* 37 (2008) 433–448.
- [29] A.V. Plyasunov, E.L. Shock, *Prediction of the vapor–liquid distribution constants for volatile nonelectrolytes in water up to its critical temperature*, *Geochimica et Cosmochimica Acta* 67 (2003) 4981–5009.
- [30] A.H. Harvey, *Applications of near-critical dilute-solution thermodynamics*, *Industrial & Engineering Chemistry Research* 37 (1998) 3080–3088.
- [31] H.B. Callen, *Thermodynamics*, John Wiley & Sons Inc, NY, 1960.
- [32] K.I. Gutkowski, R. Fernández-Prini, M.L. Japas, *Solubility of solids in near-critical conditions: effect of a third component*, *J. Physical Chemistry B* 112 (2008) 5671–5679.
- [33] D.I. Foustoukos, W.E. Seyfried Jr., *Quartz solubility in the two-phase and critical region of the NaCl – KCl – H_2O system: implications for the submarine hydrothermal systems at 9°50N East Pacific Rise*, *Geochimica et Cosmochimica Acta* 71 (2007) 186–201.
- [34] K.L. Von Damm, J.L. Bischoff, R.J. Rosenbauer, *Quartz solubility in hydrothermal seawater: an experimental study and equation describing quartz solubility for up to 0.5 M NaCl solutions*, *American J. Science* 291 (1991) 977–1007.
- [35] R.O. Fournier, R.J. Rosenbauer, J.L. Bischoff, *The solubility of quartz in aqueous sodium chloride solution at 350°C and 180 to 500 bars*, *Geochimica et Cosmochimica Acta* 46 (1982) 1975–1978.
- [36] D.R. Biggerstaff, R.H. Wood, *Apparent molar volumes of aqueous argon, ethylene, and xenon from 300 to 716 K*, *J. Physical Chemistry* 92 (1988), 1988–1994.
- [37] P.G. Debenedetti, *Clustering in dilute, binary supercritical mixtures: a fluctuation analysis*, *Chemical Engineering Science* 42 (1987) 2203–2212.

- [34] A.W. Castleman Jr., K.H. Bowen Jr., Clusters: structure, energetics, and dynamics of intermediate states of matter, *J. Physical Chemistry* 100 (1996) 12911–12944.
- [35] T.S. Zwier, The spectroscopy of solvation in hydrogen-bonded aromatic clusters, *Annual Review of Physical Chemistry* 47 (1996) 205–241.
- [36] K. Gutkowski, M.L. Japas, R. Fernández-Prini, Solubility of solids in near-critical fluids, V. CH_3I in ethane and in carbon dioxide, *J. Chemical Thermodynamics* 29 (1997) 1077–1086.
- [37] Z. Su, M. Maroncelli, Simulation of solvation free energies and solubilities in supercritical solvents, *J. Chemical Physics* 124 (2006) 164506.
- [38] G. Sciaini, E. Marceca, R. Fernández-Prini, Intermolecular solvent–solute energies for thermodynamic and spectroscopic properties of solutes in near-critical solvents, *Physical Chemistry Chemical Physics* 4 (2002) 3400–3406.
- [39] H. Destailats, R. Fernández-Prini, Solubility of I_2 and formation of I_2 charge-transfer complexes–arene in supercritical SF_6 , *J. Chemical Society, Faraday Transaction* 94 (1998) 871–878.
- [40] G. Sciaini, E. Marceca, R. Fernández-Prini, Development of the charge-transfer-to-solvent process with increasing solvent fluid density: the effect of ion pairing, *Physical Chemistry Chemical Physics* 8 (2006) 4839–4848.
- [41] M.J. Blandamer, M.F. Fox, Theory and application of charge-transfer-to-solvent spectra, *Chemical Reviews* 70 (1970) 59–93.
- [42] J.T. Nelson, R.E. Cuthrell, J.L. Lagowski, Liquid ammonia solutions. III The nature of solutions of alkali and alkaline earth iodides, *J. Physical Chemistry* 70 (1966) 1492–1495.
- [43] D. Shapira, D. Treinin, Charge-transfer-to-solvent spectra in liquid ammonia, *J. Physical Chemistry* 70 (1966) 305–306.
- [44] G. Sciaini, E. Marceca, R. Fernández-Prini, Is ammonia a better solvent than water for contact ion pairs? *J. Physical Chemistry B* 112 (2008) 11990–11995.
- [45] G. Sciaini, R. Fernández-Prini, D. Estrín, E. Marceca, Short-range and long-range solvent effects on charge-transfer-to-solvent transitions of I^- and K^+I^- contact pair dissolved in supercritical NH_3 , *J. Chemical Physics* 126 (2007) 174504.
- [46] J.-P. Hansen, K.R. McDonald, *Theory of simple liquids*, Academic Press, London, 1976.
- [47] R. Fernández-Prini, Study of local density enhancement in near-critical solutions using hydrostatic hypernetted chain theory, *J. Physical Chemistry B* 106 (2002) 3217–3225.