Proc. Indian Acad. Sci. (*Chem. Sci.*), Vol. 111, No. 2, April 1999, pp. 387–394
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Anomalous solubility of organic solutes in supercritical water: A molecular explanation

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MS received 13 October 1998

Abstract. In its supercritical state water exhibits anomalous solvent properties, the most important being its ability to solubilize organic solutes of various sizes which are sparingly soluble under ambient conditions. This phenomenon occurs at high pressure where the density is rather large (0·6–0·9 gm/cm^3). In this work, a microscopic explanation for the anomalous solubility of organic substances in supercritical water is presented by using the quasi-chemical approximation of Bethe and Guggenheim. The theory suggests the enhanced anomalous solubility arises because the critical temperature of the binary mixture (water *plus* organic solute) could be slightly lower than the gas–liquid critical temperature of pure water. Several exotic solvent properties may arise due to the subtle interplay between these two critical temperatures.

Keywords. Anomalous solubility; supercritical water; organic solutes; quasi-chemical approximation; binary solution critical temperature; interaction energies.

1. Introduction

Water seems to retain its anomalous nature even in the supercritical (SC) state which is currently under intense investigation [1–18]. While the unusual properties of water vapour were known earlier [19], the recent spurt of activity has centred around the supercritical state of this unique liquid. Amongst the most discussed properties of supercritical water are its solvation properties. Supercritical water behaves like an organic liquid with high solubility of organic compounds which are otherwise insoluble in ambient water [14]. This has generated a lot of interest because of its tremendous potential as an environmentally benign solvent for the oxidative destruction of hazardous wastes in chemical industries [20–22]. Moreover, supercritical water can be used to transform organic waste partially into light feedstocks [23].

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The critical point of water is located at $P_c = 22{\cdot}1$ MPa and $T_c = 647$ K with $d_c = 0{\cdot}32$ gm/cm^3. Most of the experimental studies on solubility in supercritical water are performed in the liquid-like density region (0·6–0·9 gm/cm^3) with the applied pressure typically in the 40–60 MPa range[24–25]. The dielectric constant of water at T_c is around 7[17]. This makes water behave like an organic solvent. Organic substances like benzene, toluene and oil have been found to be highly soluble in water at these supercritical conditions. This is certainly anomalous solvent behaviour of SC water when compared with that of normal water at ambient condition. Though this unusual solvent property of SC water has been known for sometime, it has drawn tremendous interest in the last couple of years. We are not aware of any microscopic explanation of the anomalous solvent behaviour of SC water in the literature.

In this paper we provide a very simple molecular explanation for this anomalous behaviour. This explanation comes from an analysis of the lattice model for the binary mixture of water and the organic solute[26]. In this model, both water and the organic solute are assumed to be distributed randomly at the sites of the cubic lattice. The lattice considered here is a face-centred cubic (*fcc*) one. The nearest neighbour interaction energy (average) among water molecules is denoted by ε_1 and that between organic molecules by ε_2, while the interaction energy (average) between water and organic molecules is represented by ε_{12}. Both ε_1 and ε_2 are attractive and, therefore, are of negative sign. However, what is often not realized is that the interaction between water and organic molecules can also be attractive although the magnitude of this interaction is less than ε_1 and may even be less than ε_2. The importance of this point will be made clear later. The lattice model is analysed by using the well-known quasi-chemical approximation of Bethe, Peierls and Guggenheim[26]. The results of the quasi-chemical approximation are well-known for binary mixtures. It predicts a critical temperature (T_{bc}) for phase separation. Below this temperature, the organic molecules and water separate into two distinct phases while above this temperature they are completely miscible. When we use the well-known values for the interaction energies ε_1, ε_2 and ε_{12}, we found that for the organic solutes of interest, the binary critical temperature T_{bc} falls slightly below the critical temperature T_c of water. This has led us to suggest that the anomalously large solubility of organic substances in supercritical water is a simple consequence of the subtle interplay between the two critical temperatures.

The organization of the rest of the paper is as follows. In the next section we briefly describe the lattice model and the quasi-chemical approximation. Section 3 contains the numerical results and discussion. Section 4 concludes with a brief analysis of the results.

2. Lattice model

We construct the lattice model for the binary mixture in the following way[26]. Let there be two kinds of molecules labelled '1' and '2' in the lattice system. The number of molecules of each species is denoted by N_1 and N_2 while the total number of lattice sites is denoted by $\mathcal{B}$. Let γ be the number of the nearest neighbours to each lattice site and in each lattice site there is one and only one molecule. Thus the total number of molecules in the lattice is given by N where $N = N_1 + N_2$. The number density is therefore given by $\rho = N/\mathcal{B}$. The number fractions of the two species are denoted by χ_i, equal to N_i/N where $i = 1$ and 2. In the lattice model there are clearly three different types of nearest neighbours. They are (1–1), (2–2) and (1–2) or (2–1), respectively. The last two pairs of interactions are indistinguishable from each other. If we consider only the nearest neighbour interaction,

then the energy of the system would be determined by the numbers of pairs N_{11}, N_{22} and N_{12} and the expression for the energy is given by [26],

$$E_{BM}(N_{11}, N_{22}, N_{12}) = \varepsilon_1 N_{11} + \varepsilon_2 N_{22} + \varepsilon_{12} N_{12}. \tag{1}$$

Clearly, the total energy E_{BM} of the system could be highly degenerate. The numbers N_{11}, N_{22} and N_{12} are not independent of one another. They are interrelated by the following conservation laws [26],

$$\gamma N_1 = 2N_{11} + N_{12}, \tag{2}$$

$$\gamma N_2 = 2N_{22} + N_{12}, \tag{3}$$

and

$$N_1 + N_2 = N. \tag{4}$$

Therefore, it can be shown that the total energy E_{BM} can be expressed in terms of N_{11} and N as follows [26],

$$E(N_{11}) = (\varepsilon_1 + \varepsilon_2 - 2\varepsilon_{12})N_{11} + [\gamma(\varepsilon_{12} - \varepsilon_2)N_1 + 1/2\gamma\varepsilon_2 N]. \tag{5}$$

In the quasi-chemical approximation it is convenient to introduce the long- and the short-range orders, L and σ, respectively by the following expressions [26]

$$\frac{N_1}{N} = \frac{(L+1)}{2}(-1 \le L \le +1), \tag{6}$$

and

$$\frac{N_{11}}{\gamma N/2} = \frac{\sigma+1}{2}(-1 \le \sigma \le +1). \tag{7}$$

We also introduce the notation

$$\Delta w = \varepsilon_1 + \varepsilon_2 - 2\varepsilon_{12}. \tag{8}$$

The parameter Δw turns out to be the most important parameter in the theory.

The energy of the system is then given by [26],

$$E_{B,M}(L,\sigma) = N\left[\frac{\Delta w}{4}(\sigma+1) + \frac{\gamma(\varepsilon_{12} - \varepsilon_2)}{2}(L+1) + \frac{1}{2}\gamma\varepsilon_2\right]. \tag{9}$$

The configurational partition function can be written as [24],

$$Q_N(\Delta w, T) = \Sigma g(\mathcal{B}, L, \sigma)\exp[-\beta E_{BM}(L, \sigma)], \tag{10}$$

where β is, as usual, the inverse of Boltzmann's constant (k_B) times the absolute temperature (T).

Quasi-chemical approximation makes an intuitive guess at the number $g(\mathcal{B}, L, \sigma)$. There are actually two widely different ways of arriving at the solutions. The one followed by Guggenheim was to make a binomial approximation for $g(\mathcal{B}, L, \sigma)$ [27]. This requires the approximation that the number of (1–1), (2–2) and (1–2) pairs are independent of each other. Subsequently, one obtains the term within the sum in (10) that makes the maximum contribution to the binomial coefficient. This leads to the following self-consistency conditions [26–28],

$$\left(\frac{\rho}{1-\rho}\right)^{\gamma-1}\left(\frac{1-\rho-a}{\rho-a}\right)^{\gamma/2}=\frac{1}{y}, \tag{11}$$

$$\frac{(\rho-a)(1-\rho-a)}{a^2}=\exp(2\beta\Delta\omega), \tag{12}$$

where ω denotes the number of different ways of dividing the $c\,\mathcal{B}/2$ pairs and

$$a = N_{12}/\gamma\mathcal{B}. \tag{13}$$

Analysis of these equations lead both to an equation of state and to the critical point. Below the critical point a first-order phase transition is predicted. The critical point is located at [26–28]

$$\frac{\Delta w}{2k_BT_c}=\ln\left[\frac{\gamma}{\gamma-2}\right], \tag{14}$$

where $\rho_c = 1/2$.

An alternative approach to the lattice model was developed by Bethe and Peierls [26], who derived a relation between N_{11} and N_1 by focussing attention not on the entire lattice but only on a sublattice. This approach is highly intuitive and much easier to follow. It leads exactly to the same results as those obtained from the quasi-chemical methods of Guggenheim [27–28].

The quasi-chemical approximation is exact for one-dimensional system and for higher dimensions and is superior to the often-used Bragg–William (BW) approximation [29]. The BW approximation leads to the prediction of the critical point,

$$\frac{k_BT_c}{\Delta w}=\frac{\gamma}{4}. \tag{15}$$

The BW approximation estimate of the binary critical temperature is somewhat larger than that of the quasi-chemical approximation. In this work we use the more accurate quasi-chemical approximation.

It is interesting to analyse the dependence of the binary critical temperature $T_{B,c}$ on the interaction energy parameters. When the interaction energy ε_1 and ε_2 are nearly the same and of similar nature, then ε_{12} is also expected to be close to ε_1. In this case the $T_{B,c}$ is predicted to be very small and the two components are always miscible. Another interesting scenario arises when the the solute–solvent interaction energy is attractive and

larger than either ε_1 or ε_2. In this case also the solute is completely miscible. This applies to many polar solutes or those that are capable of forming specific interaction with water molecules. Another interesting point to note is that as both the temperature and pressure are lowered towards ambient condition, the hydrogen bond (H-bond) network is restored. Since H-bond stabilization energy is larger in magnitude than the average interaction energy, ε_1 itself may increase. This would lead to further decrease in the solubility of organic solutes under ambient conditions. The situation is entirely different for organic solutes like benzene and toluene. In this case interaction energy among water molecules is somewhat larger than that among the organic solutes. We now turn our attention to the analysis of this interesting case.

3. Numerical results and discussion

As mentioned earlier, the experiments on supercritical water are usually performed at large densities. However, at the elevated temperature, the hydrogen bond network of ambient water is fully destroyed although there can be one or two hydrogen-bonds at any time around a water molecule [7,14]. Therefore, to estimate the interaction energy among water molecules we need to include the interactions between nearest neighbour water molecules (by intermolecular distance); these estimates are readily available in the literature [30]. This interaction energy consists of three different contributions. They are the electrostatic energy (U_{el}), the induction energy (U_{ind}) and the dispersion energy (U_{dis}). At 3 Å distances, these energies are −16·1 *k*J/mole, −0·9 *k*J/mole and −5·3 *k*J/mole respectively [30]. Thus, the total interaction is 22·3 *k*J/mole. If we consider benzene at nearest neighbour positions we need to consider carbon–carbon and carbon–hydrogen interactions and also the quadrupolar interactions between two benzene molecules. When all these interactions are included, this leads to a value of $\varepsilon_2 = 14$ *k*J/mole [31].

We first discuss the case of benzene in water. We consider the lattice to be an *fcc* lattice with $\gamma = 12$. Use of (14) leads to a critical temperature of the mixture (T_{bc}) equal to 550 K. This is lower than the gas–liquid critical temperature (T_c) of pure water which is 647 K. Thus, benzene is predicted to be soluble in water *above* ~ 550 K. This is shown schematically in figure 1.

We next consider the case of water and toluene. As the toluene-toluene interaction is somewhat larger than that between benzene, the theory predicts that toluene will be *less soluble* in supercritical water than benzene. This is again in accordance with experimental observations [9–10].

It is also interesting to consider the case of cyclohexane. Here ε_{12} is expected to be smaller than those for benzene and toluene. The quasi-chemical prediction is that cyclohexane will be even less soluble than benzene and toluene at a temperature below the critical point, T_c.

On the other hand, if one considers a protic system like phenol then both $\varepsilon_{\text{phenol–phenol}}$ and $\varepsilon_{\text{phenol–water}}$ will register an increase. Therefore, Δw will decrease and phenol is predicted to be miscible at temperature lower than the benzene–water system which is indeed the case.

It is interesting to note that while the gas–liquid critical temperature (T_c) is *constant* for a particular liquid, the critical solution temperature of a binary mixture (T_{bc}) *varies* depending upon the solute–solute and the solute–solvent interaction strengths. Thus, depending upon the magnitude of Δw (given by (8)), T_{bc} can fall either above or below T_c. For many organic solutes, these two critical temperatures may be close to each other as shown *schematically* in figure 1.

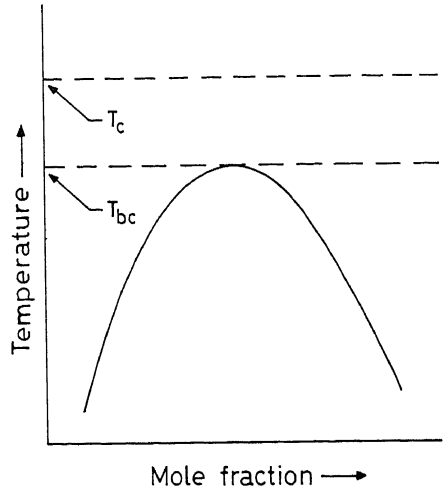

Figure 1. A schematic diagram of the temperature-composition curve for a two-component binary mixture. The temperature of a mixture of water and an organic solute is plotted as a function of mole fraction of the organic solute. The solid line indicates the phase separation line above which both the components are completely miscible. The critical temperature of water is 647 K which is shown as T_c. The critical solution temperature of the binary mixture is denoted by T_{bc}. Note that the location of T_{bc} on the temperature axis can vary depending upon the nature of the solute whereas that of T_c is fixed. For discussions, see text.

It is important to note that the quasi-chemical approximation provides a very simple picture of hydrophobicity which arises because water–water interaction is stronger than the interaction among water and organic molecules. The water–organic solute interaction *need not be repulsive*. Thus the organic solutes are not really water–repulsive. Rather, it is the water that *likes itself much more than the organic solute*. The phase separation between water and organic solute is driven by the relative difference among the interaction energies which, at low temperature, wins over the entropic force that tries to homogenize the system.

For the organic solutes of interest here (benzene, toluene and cyclohexane) the binary critical point is quite high. This guarantees that the solubilities of these solutes in ambient water are negligible. This is expected on general grounds.

4. Conclusion

The anomalously large solubility of some organic solutes in supercritical water appears to be surprising at first sight because the density of water remains rather large under the experimental conditions. In this work we presented a lattice model for binary mixtures which, when analysed by the quasi-chemical method of Guggenheim and Bethe, predicts a binary critical temperature which is smaller than but comparable to that of pure ambient water. This provides a simple physical explanation of the large solubilities of organic solutes in supercritical water.

The present analysis needs to be improved upon by using a more accurate theory, such as the density functional theory (that is, the generalized Ginzberg–Landau approach)[32] which is common in the treatment of binary mixtures. In particular, one needs to include the size disparity between the solute and the solvent molecules. However, the simplicity and the transparency of the lattice model and the quasi-chemical model makes it a useful tool for the study of the phase separation problem. It is particularly pleasing to see the simple and elegant expression that the quasi-chemical approximation provides for the hydrophobicity or hydrophilicity of organic molecules.

Acknowledegment

We thank Dr S Yashonath for useful discussions. The authors are also thankful to Professors P Rossky and A Nitzan for informative discussions. The work reported here has been supported in part by grants from the Council of Scientific and Industrial Research (CSIR), India and the Department of Science and Technology (DST), India. RB thanks CSIR for a fellowship.

References

1. Eckert C A, Fknutson B L and Debenedetti P G 1996 *Nature (London)* **383** 313
2. Seewald J S 1994 *Nature (London)* **370** 285
3. Postorino P, Tromp R H, Ricci M A, Soper A K and Neilson G W 1993 *Nature (London)* **366** 668
4. Mango F D, Highwater J W and James A T 1994 *Nature (London)* **368** 536
5. Shock E L 1994 *Nature (London)* **368** 499
6. Price L C 1994 *Nature (London)* **370** 253
7. Hoffman M M and Conradi M S 1997 *J. Am. Chem. Soc.* **119** 3811
8. Prini R F and Japas M L 1994 *Chem. Soc. Rev.* **23** 155
9. McHugh M A and Krukonis V J 1986 In *Supercritical fluid extraction: Principles and practice* (Boston, MA: Butterworth)
10. Kim S and Johnston K P 1987 In *Supercritical fluids, chemical and engineering principles and applications* (eds) T G Squires and M E Paulatis (ACS Symposium Series 329) (Washington, DC: Am. Chem. Soc.)
11. Ricci M A, Nardone M, Fontana F, Andreani C A and Hahn W 1998 *J. Chem. Phys.* **108** 450
12. Funel M C B, Tassing T, Zhao H, Beysens D, Guillot B and Guissani Y 1997 *J. Chem. Phys.* **107** 2942
13. Brock E E, Oshima Y, Savage P E and Barker J R 1996 *J. Phys. Chem.* **100** 15834
14. Matubayasi N, Wakai C and Nakahara M 1997 *J. Chem. Phys.* **107** 9133
15. Kalinichev M and Bass J D 1997 *J. Phys. Chem.* **A101** 9720
16. Wallen S L, Palmer B J, Pfund D M, Fulton J L, Newville M, Ma Y and Stern E A 1997 *J. Phys. Chem.* **A101** 9632
17. Okada K, Imashuku Y and Yao M 1997 *J. Chem. Phys.* **107** 9302
18. Luo H and Tucker S 1996 *J. Phys. Chem.* **100** 11165
19. Franks F (ed.) 1982 In *Water: A comprehensive treatise* (New York: Plenum) vol. 7
20. Shaw R W, Brill T B, Clifford A A, Eckert C A and Franck E U 1991 *Chem. Eng. News* **69** 26
21. Harradine D M, Buelow S J, Dell'Orco P C, Dyer R B, Foy B R, Robinson J M, Sanchez J A, Spontarelli T and Wander J D 1993 *Haz. Waste Haz. Mater.* **10** 233
22. Killilea W R, Swallow K C and Hong G T 1992 *J. Supercrit. Fluids* **5** 72
23. Elliott D C, Phelps M R, Sealock L J Jr and Baker E J 1994 *Ind. Eng. Chem. Res.* **33** 566
24. Peck D G, Mehta A and Johnston K P 1989 *J. Phys. Chem.* **93** 4297
25. Johnston K P and Haynes C 1987 *AIChE J.* **33** 2017
26. Huang K 1991 *Statistical mechanics* (New Delhi: Wiley-Eastern) chap. 16
27. Guggenheim E A 1952 *Mixtures* (London: Oxford)
28. Hill T L 1987 *Statistical mechanics* (New York: Dover) chap. 7

29. Bragg W L and Williams E J 1934 *Proc. R. Soc.* **A145** 699
30. Rigby M, Smith E B, Wakeham W A and Maitland G C 1986 *The forces between molecules* (Oxford: Clarendon) chap. 1
31. Linse P 1984 *J. Am. Chem. Soc.* **106** 5425; Linse P, Engstrom S and Jonsson B 1985 *Chem. Phys. Lett.* **115** 95
32. Hohenberg P C and Halperin B I 1977 *Rev. Mod. Phys.* **49** 435