Influence of thermodynamic variables and molecular parameters in the solubility of gases in liquids

Roberto Fernández Prini

Departamento Química de Reactores, Comisión Nacional de Energía Atómica and Departamento Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires.

Abstract – A semiempirical procedure based upon measurements of solubility over a reduced temperature range and the use of a perturbation method with a hard-sphere reference fluid, is able to describe satisfactorily the thermodynamics of dissolution of nonpolar gases in water over all the temperature range and for gas pressures up to 50 MPa. The procedure can also be applied to systems constituted by anisotropic molecules, either sphericallizing the intermolecular potential or employing the interaction site model. The possibility of extending these ideas to deal with the dissolution of gases exhibiting larger intermolecular interactions with the solvent is explored.

INTRODUCTION

The study of the solubility of nonpolar gases in liquids has been the basis upon which many ideas about the Physical Chemistry of Solutions have been laid. The introduction of a nonpolar unreactive gas particle into a dense fluid involves a relatively small change in the interactions already prevailing in the liquid. It is scientifically relevant to inquire into the factors which determine the thermodynamic quantities characterizing this process. Also in many applied fields of Chemistry, Biochemistry, Chemical Technology and Geochemistry there is interest in the thermodynamic description of gas-liquid binary systems. On both accounts aqueous solutions of gases play a prominent role.

The theoretical description of the thermodynamics of dissolution of gases in liquids over a wide range of values of the state variables (<u>i.e.</u>, temperature, pressure, densities) is a plausible goal due to progress in the Statistical Mechanics of dense fluids. It is possible to use models and develop calculation procedures which, in principle, are able to deal with any liquid solvent, thus eliminating the artificial, albeit practical, distinction between aqueous and nonaqueous solvents.

I shall try to summarize in this work the features of a calculation procedure employed in our laboratory to describe the thermodynamics of dissolution of gases in liquids, and then discuss its advantages and its limitations. The method is capable of describing the behaviour over wide ranges of the thermodynamic variables and for systems with different types of molecular interactions.

MODEL AND CALCULATION PROCEDURE

The adopted model has been used by Ely in 1939 (ref. 1) to describe the thermodynamic features of the dissolution of gases in liquids. The dissolution of the gas molecules is represented by a two-step process, first a cavity large enough to host the solute molecule is made in the solvent and then the interactions between solvent and solute are switched on. In 1963 Pierotti (ref. 2) employed successfully the same model to calculate the thermodynamic properties of gases dissolved in aqueous and nonaqueous solvents around room temperature employing scaled particle theory.

Using gas solubility data it is possible to determine Henry's constant, $k_H^\infty(T)$; its logarithm is related to the difference of standard chemical potential of the solute in the liquid solvent and in the gas phase, $\Delta\mu_2^\infty$. Thus for the dissolution process,

$$\Delta\mu_2^\infty = RT \ln \frac{k_H^\infty(T)}{p^\ominus} = \mu_2^{ref} + \mu_2^{att} + RT \ln (\rho_1^* RT) \tag{1}$$

where ρ_1^* is the solvent density, μ_2^{ref} is the work of cavity formation (reference term) and μ_2^{att} is the contribution of the attractive interactions between solvent and solute. The dissolution process described by (1) is ideally suited to use a perturbation method in order to calculate its thermodynamic properties: the reference term corresponding to the dissolution of a hard-sphere solute, and the perturbation being the solute-solvent intermolecular interaction (essentially attractive Lennard-Jones).

A completely rigorous calculation of properties of solutions with this procedure is limited because there are approximations inherent to the perturbative expansion (lambda-expansion) and to the equations used for the equivalent fluid (reference fluid) (ref. 3). Moreover, if employed to describe <u>real</u> systems the greatest problem is the fact that perturbation methods are extremely sensitive to the values of the molecular parameters (energy and size), being strongly affected by the usual uncertainty of these parameters. The terms in eq. (1) are given by (ref. 4),

$$\underline{\mu}_2^{ref} = -RT\ \ln(1-y)\ +\ 2\pi\rho_1^* RT\ \int_0^{d_2} G^o_{12}\ (z)z^2 d\underline{d}_2\ ;\ z = \frac{d_1 + d_2}{2} \tag{2}$$

and

$$\underline{\mu}_2^{att} = 4\pi\rho_1^* \int u'_{12}\ (r)g^o_{12}\ (r)r^2\ dr \tag{3}$$

where $g^o_{12}(r)$ is the radial distribution function of the references fluid particles which surround a solute molecule, G^o_{12} its value at contact, and $u'_{12}(r)$ is the perturbation of the solute-solvent intermolecular energy. Due to the limitations mentioned above, μ_2^{att} is restricted in eq. (3) to the first order contribution; hence the calculation procedure becomes semiempirical, but conditioned to the use of molecular parameters which may also account for other properties of the studied systems. The term μ_2^{ref} is that corresponding to a hard-sphere equivalent fluid with the (number)density of the actual solvent. In (2) and (3) we use the Percus-Yevick (PY) equations for the reference hard-sphere fluids (ref. 5 and 6), they provide the correct framework to calculate other thermodynamic properties and a sound basis to relate these with molecular parameters. Furthermore, using the PY approximation it is possible to extend the treatment to systems with anisotropic molecules.

The equivalent hard-sphere diameters are given to a first approximation by (ref. 3),

$$\underline{d}_i = \int [1\ -\ \exp\ (-\ \frac{u^o_{ii}\ (r)}{kT})]\,dr \tag{4}$$

where $u^o_{ii}(r)$ is the soft repulsive unperturbed intermolecular potential which is replaced in the reference fluid by an equivalent hard-sphere potential. This equation was used only when $u^o_{ii}(r)$ could be represented by the Lennard-Jones equation, otherwise $\underline{d}_i$ was an adjustable parameter, <u>i.e.</u> for aqueous systems. The PY expressions for (2) and (3) (ref. 6) indicate that $\Delta\mu_2^\infty$ depends on the packing fraction of the solvent $y = \pi\rho_1^* d^3/6$, on the ratio of solute to solvent diameters and on the Lennard-Jones parameters.

AQUEOUS SOLUTIONS OF NONPOLAR GASES

In order to describe the dissolution of gases in water up to its critical point, it is necessary to make a thorough and careful analysis of the solubility data. The gas solubility, expressed by the solute's mole fraction $\underline{x}$, and its fugacity, $\underline{f}_2$, are related to Henry's constant by,

$$\ln\ \frac{f_2}{xp^\ominus}\ =\ \ln\ \frac{k_H^\infty}{p^\ominus}\ +\ \int_{p_1^*}^p\ \frac{v_2^\infty}{RT}\ dP\ +\ \ln\ f_2^H \tag{5}$$

where V_2^∞ is the solute partial molar volume at infinite dilution and f_2^H the solute activity coefficient. The last two terms in eq. (5) give corrections to the solute chemical potential due to an increase in pressure (Poynting correction) and to solute-solute interactions respectively. When the temperature of the dilute solution is close to the critical

temperature of the solvent (T_{1c}), both contributions become very important, actually V_2^∞ tends to $+\infty$ at T_{1c}. The PY perturbation method affords a means of calculating self-consistently these two corrections (ref. 7), and hence to determine k_H^∞ from gas solubilities, pressure and temperature.

Another point worth remarking is that the PY equation provides a means to calculate other thermodynamic quantities of dissolution by differentiation of $\Delta\mu_2^\infty$. The polynomials which are normally employed to represent the temperature dependence of $\ln(k_H^\infty/p^\ominus)$, when directly differentiated do not give the right answer over a wide temperature range (ref. 6). Figure 1 compares the calorimetric data for $\Delta C_{p,2}^\infty$ of Ar in water (ref. 8) with values obtained by differentiation of two polynomials in temperature which are often employed to represent the k_H^∞ data. These polynomials may be expressed by,

$$\ln \frac{k_H^\infty}{p^\ominus} = B \frac{T_{1c} - T}{T} \ln(\frac{T_{1c} - T}{T_{1c}}) + \Sigma_i \frac{A_i}{T^i} \tag{6}$$

It is clear that the values of $\Delta C_{p,2}^\infty$ obtained with the PY equations agree with the calorimetric data, while those obtained by differentiation of eq. (6) fail dramatically above 450 K, even after proper thermodynamic correction.
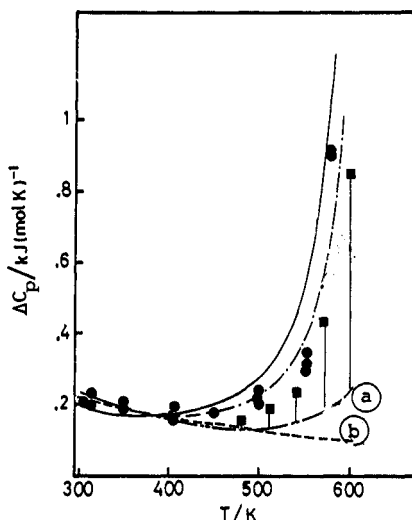

Fig. 1. $\Delta C_{p,2}^\infty$(Ar,aq) against temperature. Curves obtained by differentiation of: (a) eq. (6), (b) eq. (6) with B=0. ■: correction to isobaric conditions. Calculated with PY procedure; ———: vapour pressure, —·—·: 17.2 MPa. Calorimetric data: ● .

In the calculation procedure applied to aqueous solutions, we use $\underline{d}_1 = 0.27$ nm at all temperatures and values for ε_{22} and $\sigma_2 = \underline{d}_2$ taken from the literature. With the PY expression for eq. (1), $\varepsilon_{11} = (\varepsilon_{12}^2/\varepsilon_{22})$ was calculated from the solubilities of inert gases, H_2, N_2, O_2, CH_4 and C_2H_6 in water at 298 K; it was found that $(\varepsilon_{11}/k) = 217$ K. ε_{11} is the Lennard-Jones water-water intermolecular energy, i.e. when hydrogen bonding and dipole-dipole contributions are eliminated. The value of ε_{11}/k calculated from cross-term second virial coefficient data for binary gaseous mixtures of water and nonpolar gases was 220±10 K (ref. 9), which agrees very well with that obtained from gas solubility. Henry's constants for these gases are correctly reproduced over all the temperature range if $\underline{d}_2$ is assumed to decrease linearly with temperature (ref. 6).

In order to judge the overall performance of this method it is necessary to calculate from k_H^∞ the solute distribution factor, $\underline{K}_D^\infty = \text{Lim}(\underline{y}/\underline{x})$ ($\underline{i.e.}$ mole fraction ratio of solute in the $x \to 0$ vapour to that in the liquid). These two quantities are related by $\underline{k}_H^\infty = \underline{K}_D^\infty \phi_2^\infty \underline{p}_1^*$, where ϕ_2^∞ is

the fugacity coefficient of the solute at infinite dilution in the gas phase and p_1^* is the solvent vapour pressure. Japas and Levelt Sengers (ref. 10) have shown that the relation,

$$T \ln K_D^\infty = A(\rho_1^* - \rho_{1c}^*) \tag{7}$$

must be obeyed by liquid-vapour equilibrium close to T_{1c}. Figure 2 illustrates the performance of the method applied iteratively to the system N_2-H_2O studied up to 636 K (ref. 7). It is seen that the procedure is self-consistent and complies with eq. (7), $T.\ln(K_D^\infty)$ extrapolates to the critical density of water ρ_{1c}^* only if the Poynting effect and the activity coefficient contributions are taken into account.

As consecuence of these observations the use of a simplified procedure to describe the dissolution process has been suggested. This couples experimental solubility measurements over a reduced temperature range (where good experimental precision is attained) with K_D^∞ obtained by extrapolation with eq. (7) for the higher temperatures. The PY perturbation method is then used to obtain the temperature dependence of d_2 over all the temperature range, this is the only adjustable parameter upon which the properties of the solutions depend. The performance of this procedure may be assessed with data for C_2H_4-H_2O (ref. 11 and 12). As shown in Fig. 3 the agreement is good, especially considering the restricted
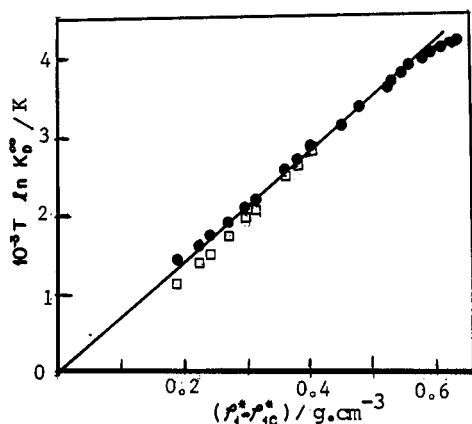

Fig. 2. $T \ln(K_D^\infty)$ against solvent density for N_2 dissolved in water. Experimental points with full correction, ● ; without correction for activity coefficients, □ .

temperature range (60 K) over which data for the solubility of ethylene in water exist. This limited experimental information introduces uncertainty in the precise dependence of d_2 upon temperature (the hatched areas in Fig. 3 cover this ambiguity).
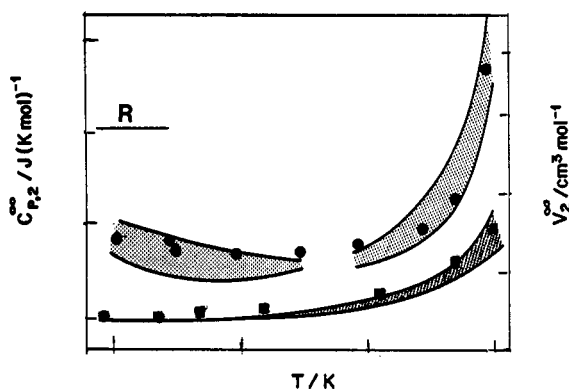

Fig. 3. C_2H_4 dissolved in H_2O. ● : $\Delta C_{p,2}^\infty$ and ■ : V_2^∞. Curves and hatched areas: calculated with PY procedure R: temperature range of available solubility data.

What can be said of the use of a hard-sphere reference fluid to describe aqueous solutions where the solvent exhibits anomalous behaviour due to the strong positional and orientational correlation existing among neighbouring H_2O molecules? It is convenient to compare the PY perturbation method to a semiempirical method proposed by Pratt and Chandler (PC) (ref. 4) which uses <u>real</u> water as the reference fluid. In order to obtain $g_{12}^o(r)$, which is necessary to calculate $G_{12}^o(z)$ in eq. (2), Pratt and Chandler employed the Ornstein–Zernike equation for the infinitely dilute solution which relates $g_{12}^o(r)$ to the radial distribution function of pure water;

$$g_{12}^o(r) - 1 = c_{12}^o(r) + \rho_1^* \int c_{12}^o(r) \, (g_{11}(r) - 1) \, dr \qquad (8)$$

where $c_{12}^o(r)$ is the solvent-solute direct correlation function. The radial distribution function of water, $g_{11}(r)$, is obtained from X-ray or neutron scattering experiments in pure water. Thus $g_{12}^o(r)$ retains all the features of water structure. For dilute solutions of nonpolar gases this PC perturbation method yields very similar results to that of PY (ref. 13). Figure 4 is a plot of the radial distribution function (g_{12}^o) of solvent surrounding a hard-sphere solute of 0.4 nm diameter when the solvent is either water or a hard-sphere equivalent fluid. It is seen that for the hard-sphere solute at infinite dilution the first layers of solvent look the same whether it is H_2O or a hard-sphere fluid with the same packing fraction, the number of nearest neighbour solvent particles surrounding a solute particle, is the same in both fluids. Since the nonpolar solute-solvent interactions are weak and short-ranged, the contribution of the nearest neighbours molecules is the only significant one.
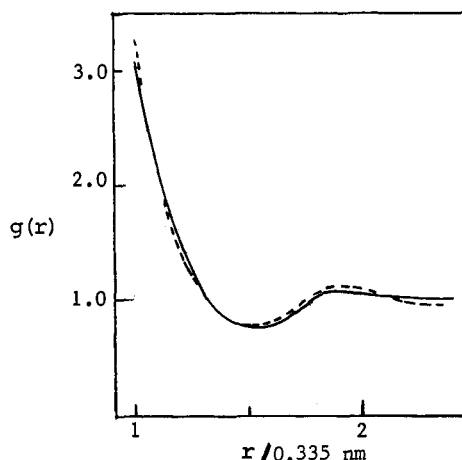
Fig. 4. Radial distribution function of solvent surrounding a hard-sphere of 0.4 nm at infinite dilution: ---: PY; ——: PC.

ANISOTROPIC NONPOLAR SOLVENT MOLECULES

The calculation procedure outlined above may seem better suited to deal with nonpolar solvents because their molecules only interact through dispersive forces. However, this proved not to be the case. Table 1 gives the difference between the $\Delta\mu_2^\infty/RT$ of Ar and those of Kr, Xe and CH_4 in benzene. The effects of an increase in solute diameter and in ε_{22} is not correctly predicted by the hard-sphere PY calculation procedure. Since for nonpolar gases like Ar or CH_4, the molecules of typical nonpolar solvents such as CCl_4, C_6H_6 or liquid alkanes, appear strongly non-spherical, it was considered important to inquire if the disagreement was due to the anisotropy of the solvent molecule.

Sphericallized intermolecular potentials

One way of extending the calculation procedure described above to these solutions taking into account molecular anisotropy, is to sphericallize the intermolecular potentials (ref. 14). It was observed that the contribution of the anisotropic molecules to the effective

minimum energy (ε_{min}) of the sphericallized potentials, depends on the relative sizes of the two interacting molecules. In other words, the value of ε_{11} used to calculate $\varepsilon_{min} = \varepsilon_{12} = (\varepsilon_{11}\ \varepsilon_{22})^{1/2}$ which is contained in $u'_{12}(r)$, will change with solute size.

This is illustrated in Fig. 5 for two different sphericallization procedures applied to the interactions of a diatomic homonuclear molecule with a spherical particle.

TABLE 1. $\dfrac{\Delta\mu_2^{\infty}(Ar)}{RT} - \dfrac{\Delta\mu_2^{\infty}(X)}{RT}$ in benzene at 298 K.

X	PY	Sph	ISM	Exp.
CH_4	0.255	0.557	0.711	0.857
Kr	0.704	---	1.282	1.136
Xe	0.837	1.881	2.418	2.582

Table 1 also reports the results of the sphericallization (Sph) of intermolecular potential employing the median criterion, it is clear that sphericallization partially resolves the discrepancy observed with the hard-sphere PY procedure. Sphericallization of the intermolecular potentials is a practical and convenient solution, but limited to systems with molecules which are not very anisotropic.
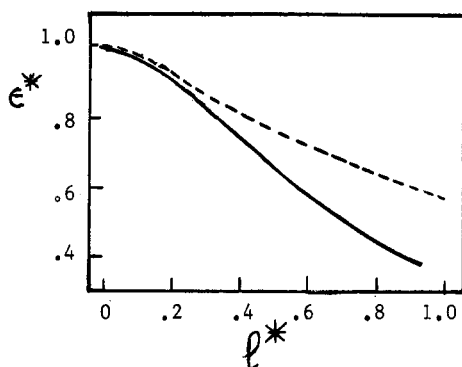

Fig. 5. $\varepsilon^* = (\varepsilon_{11}/2\varepsilon_s)$ against $\underline{1}^* = 2\underline{1}$ (d_s+d_2) for interaction of a dumbell with site parameters ε_s and d_s and distance $\underline{1}$ between sites and a spherical Lennard-Jones molecule of diameter d_2. Sphericallization procedure: ———, RAM; ---, median.

The interaction-site method

In order to improve upon the result of sphericallization, we have used an interaction site model (ISM) (ref. 15) which represents molecules by a succession of spherical sites, thus it was possible to deal fairly rigorously with anisotropic molecules under the PY approximation. We have studied C_6H_6 and n-alkanes as solvents, these molecules were considered formed by one type of site only. The energy and size site parameters were obtained from the solvent's vapour pressure, because when the molecular parameters of the solute are the same as those of the solvent, eq. (1) gives the "chemical potential of dissolution" of a solvent molecule in the liquid solvent itself. Consequently, in eq. (1) $k_H^{\infty}(T)$ is replaced by $\underline{f}_1^*$, the fugacity of the pure solvent, and the perturbation procedure may be used to calculate the solvent site parameters. For n-butane over a temperature interval of 75 K, the site energy was 102.1±.5 K and the diameter 0.392 nm, values which were used for the other n-alkanes. For C_6H_6 the site energy was 84.3±.2.2 K and its diameter 0.372 nm for a temperature interval of 150 K. Details of the ISM calculation will be reported elsewhere (ref. 16).

With the values of the interaction site energy (ε_s) of the solvent, binary systems were studied. Table 1 reports the change of $\Delta\mu_2^{\infty}/RT$ when going from Ar to Xe dissolved in benzene

as calculated with the ISM, the predicted changes of solubility are close to the experimental values. Therefore a significant improvement is obtained using the PY-ISM method.

It is more difficult to calculate the individual $\Delta\mu_2^\infty$ values without adjusting any parameter. The values of ε_s/k necessary to fit the $\ln(k_H^\infty/p^\ominus)$ data were calculated for inert gases and methane in various solvents at 298 K. For benzene ε_s/k was 89±3 K and for pentane, hexane and heptane, ε_s/k = 91±4 K, the uncertainties in ε_s imply and uncertainty of 8 to 15% in the predicted solubilities.

SOLUTES WITH STRONGER INTERACTIONS WITH SOLVENTS

We turn now to consider aqueous binary systems where the solutes are dipolar or have some degree of hydrogen bonding to H_2O, in order to find out if the perturbation method may be extended to deal with substances having somewhat stronger interactions with the solvent. For this analysis, molecules were considered spherical. In Table 2 various gaseous solutes are considered and the values of the parameters which fit the (low temperature) solubility data (s) are compared to those obtained from pure gaseous solutes (g) and from cross-second virial coefficients of the gases and water vapour (v) (ref. 17). For CO, CO_2 and N_2O, the interaction energy (ε_{11}/k) obtained was greater than 217 K because hydrogen bonding contributes to a certain extent, but it had the same value for binary mixtures in gas and liquid phases.

Table 2. Molecular Parameters for Binary Aqueous Mixtures

Solute gas	ε_{22}/k K	$_2, \underline{d}_2$ nm	μ_2 debye	ε_{11}/k K	
CO	100	0.376	0.11		g
	100	0.376	--	266	v
	100	0.353	--	266	s
N_2O	189	0.459	0.17		g
	189	0.459	--	385	v
	189	0.450	--	385	s
CO_2	189	0.449	--		g
	189	0.449	--	385	v
	189	0.427	--	385	s
CH_3F	207	0.336	1.82		g
	207	0.343	--	302	s
CH_3Cl	318	0.344	1.87		g
	318	0.344	1.87	217	v
	318	0.343	--	217	s

For dipolar gases it is possible to use a Lennard-Jones intermolecular potential to represent the interactions if the molecular parameters are redefined in terms of dipole moments and polarizabilities (ref. 5). In this way the PY hard-sphere formalism may be maintained. The results in Table 2 for FCH_3 and $ClCH_3$ show that solubilities may be correctly predicted if these solutes are considered nonpolar (*i.e.* if ε_{22} is that corresponding only to dispersive forces), otherwise predicted solubilities are much larger than the experimental ones. It is as if the collective effect of solvent dipoles in the liquid phase partially cancelled the contribution of the solvent electric field on the solute particle.

CONCLUSIONS

The dependence of the properties of dilute solutions of gases in liquids on the state variables and on the molecular parameters of the solutes is correctly represented by the perturbation procedure used. However, in spite of the general success of the method, the individual terms of μ_2^{ref} and μ_2^{att} are much larger than $\Delta\mu_2^\infty$ and have opposite sign, so that

an important part of their contributions cancels out. This is the reason for the extreme sensitivity of calculated $\Delta\mu_2^\infty$ upon the solute's energy parameter. It must be considered that the intermolecular parameters for inert gases are known within 1% (ref. 18); furthermore, to a certain extent they are property dependent (ref. 5). So that in spite of the good description afforded by the perturbation method, the uncertainty in the molecular parameters involves errors which are much larger than the experimental precision of solubility data. As an example, for CH_4 the values usually quoted for ε_{22}/k are 157±10 K, this uncertainty implies a 35% uncertainty in k_H^∞. Since there is no way of knowing the molecular parameters with the level of precision required by the experimental solubility data, it is convenient to use the method semiempirically because then the properties of the infinitely dilute solution may be predicted satisfactorily with minor adjustments of the molecular parameters.

The extensions of the perturbation procedure to systems constituted by anisotropic molecules or having stronger intermolecular interactions, show that also for these systems the PY perturbation equations give the correct dependence of thermodynamic quantities on the state variables and on the molecular parameters. However also for these systems to get good agreement, ε_s and the temperature dependence of $\underline{d}_2$ should be adjusted empirically.

REFERENCES

1. D.D. Ely, Trans. Faraday Soc., 35, 1281, 1421 (1939).
2. R.A. Pierotti, J. Phys. Chem., 67, 1840 (1963).
3. L. Verlet and J-J. Weis, Phys. Rev. A, 5, 939 (1972).
4. L.R. Pratt and D. Chandler, J. Chem. Phys., 67, 3683 (1977).
5. T.M. Reed and K.E. Gubbins, Applied Statistical Mechanics, MacGraw-Hill Kogakusha, Tokyo 1973.
6. R. Fernández Prini, High Temperature Aqueous Solutions: Thermodynamic Properties, CRC-Press, 1990.
7. J. Alvarez and R. Fernández Prini, to be published.
8. B.R. Biggerstaff, D.E. White and R.H. Wood, J. Phys. Chem., 89, 4376 (1985).
9. J. Alvarez, R. Crovetto and R. Fernández Prini, Z. physik. Chem. (N.F.), 136, 135 (1983).
10. M.L. Japas and J.M.H. Levelt Sengers, AIChe J. 35, 705 (1989).
11. E. Wilhelm, R. Battino and R.J. Wilcock, Chem. Rev., 77, 219 (1977).
12. D.R. Biggerstaff and R.H. Wood, J. Phys. Chem., 92, 1988, 1994 (1988).
13. R. Fernández Prini, R. Crovetto, M.L. Japas and D. Laría, Acc. Chem. Res., 18, 207 (1985).
14. R. Fernández Prini and M.L. Japas, J. Chem. Phys., 85, 2951 (1986).
15. D. Chandler, in The Liquid State of Matter, eds. E.W. Montroll and J.L. Lebowitz, North-Holland, 1982, p. 275.
16. D. Laría and R. Fernández Prini, to be published.
17. C.J. Wormald and N.M. Lancaster, J. Chem. Soc. Faraday I, 84, 3141 (1988).
18. P.A. Egelstaff, Faraday Disc. Chem. Soc., 66, 7 (1978).