Bull. Chem. Soc. Jpn., 73, 2445—2452 (2000)

Solubility Prediction Using Statistical Mechanics

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(Received December 3, 1999)

In the present work, a new expression for the chemical potential of a component in its pure and mixed state has been derived using the classical partition function and the Linear Isotherm Regularity, LIR. Using this approach, we are able to interpret all contributions of ideal and non-ideal terms which appear in the chemical potential. The derived chemical potential satisfies Raoult's and Henry's laws. We may also predict the solubility using the chemical potential without any adjustable parameter when the solvent and solute have molecular similarity, like NH_3 in H_2O. However, for cases in which the solvent and solute molecules are significantly differ, one adjustable parameter must be considered. Success in predicting the solubility in different systems is due to the generality of the used equation of state, LIR.

Predicting solubility is a main point in chemical process design and, recently, in supercritical fluid technology. An experimental determination of solubility is not an easy task for hazardous solvents, or for a medium under extreme temperature and/or pressure. Therefore, using an accurate solubility equation can yield satisfactory information without involving any experimental difficulties.

Recently, there has been considerable progress in the development of an analytical statistical-mechanical equation of state applicable for deriving a solubility equation. Kwak and Mansoori[1] developed a mixing rule for a cubic equation of state based on statistical mechanical theory from which the solubility of heavy solids in supercritical fluids may be predicted. They used such a prediction as a sever test for the mixture equation of state. Although their prediction of the solubility versus pressure is in better agreement with the experimental data than the original mixing rule, this success is partly indebted to additional adjustable parameters. Mohsen-nia et al.[2] introduced two new constant parameters for their cubic equation of state. They have claimed that their equation is more accurate than the Redlich–Kwong equation of state in predicting the properties of pure fluids and fluid mixtures, including the solubility.

Our aim in this work is to predict the solubility in dense fluids, with densities greater than the Boyle density, using classical statistical thermodynamics and the linear isotherm regularity, LIR, as an equation of state. In this article, we first introduce the LIR, and then derive an expression for the chemical potential of a component in both pure and mixed phases. Finally, we predict the solubility of some components in given solvents using the equality of chemical potential of that component in two phases at a fixed temperature and pressure.

Linear Isotherm Regularity

Recently, a general regularity was reported for pure dense fluids,[3] according to which $(Z-1)v^2$ is linear with respect to ρ^2 for each isotherm for densities greater than the Boyle density and temperatures lower than twice the Boyle temperature. Thus,

$$(Z-1)v^2 = A + B\rho^2, \tag{1}$$

where Z is the compressibility factor and $\rho = 1/v$ is the molar density; A and B are temperature dependent parameters, as follows:

$$A = A'' - A'/RT \tag{2a}$$

and

$$B = B'/RT. \tag{2b}$$

A' and B' are related to the intermolecular attractive and repulsive forces, respectively, while A'' is related to the non-ideal thermal pressure. This regularity is also valid for dense mixtures as well as pure fluids. The composition dependencies of the parameters were obtained as their temperature dependencies.[4] The temperature dependencies for a mixture parameters are as follows:

$$A_{\text{mix}} = A''_{\text{mix}} - A'_{\text{mix}}/RT, \tag{3a}$$

$$B_{\text{mix}} = B''_{\text{mix}} + B'_{\text{mix}}/RT, \tag{3b}$$

and their composition dependencies are

$$B_{\text{mix}} = \sum_{i,j} B_{ij} x_i x_j, \tag{4a}$$

$$(A/B)_{\text{mix}} = \sum_{i,j} (A/B)_{ij} x_i x_j, \tag{4b}$$

where the coefficients for $i = j$ are for the pure components and $i \neq j$ for a hypothetical mixture with only the $i-j$ interaction. For many binary mixtures, the unlike LIR parameters ($i \neq j$) are taken as the mean geometric of those for pure parameters,[5]

$$(A/B)_{12} = [(A/B)_{11}(A/B)_{22}]^{1/2}, \tag{5a}$$

$$B_{12} = (B_{11}B_{22})^{1/2}. \tag{5b}$$

Chemical Potential for a Component in the Pure State

Many chemical phenomena depend on the properties of a solution, and much of our knowledge about such properties arises from the studies of the equilibrium state. For example, knowledge concerning the chemical potential of a substance is needed to develop a quantitative description of solubility. It should therefore be obvious that the first step in studying the thermodynamics of a solution is to determine the functional dependencies of the chemical potential of the solute on the composition, temperature, and pressure or density.

In this study, we obtain an expression for the chemical potential using the Linear Isotherm Regularity and the classical statistical partition function. We first start with the partition function for the canonical ensemble ($Q(T,V,N)$),

$$Q(T,V,N) = \frac{q^N}{\Lambda^{3N} N!}\int \dots \int e^{-\beta U_N} \mathrm{d}R_1 \dots \mathrm{d}R_N, \tag{6}$$

where, q, N, Λ^3, and U_N are the internal partition function of a single molecule, the number of particles, the momentum partition function, and the configurational potential energy, respectively and $\beta = 1/kT$ has its usual meaning. The chemical potential is related to the partition function as

$$\mu = -kT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V} \tag{7}$$

Using the Stirling approximation for the ideal-gas behavior, $U_\mathrm{N} = 0$, we simply find the chemical potential to be

$$\mu = -kT\ln q + kT \ln \frac{N\Lambda^3}{V}, \tag{8}$$

where V is the volume. As shown in Eq. 8, two terms are included in the ideal-gas chemical potential which may be interperatated by using the Helmholtz free energy. To do so, we present the chemical potential in T, V, N space as

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = A(T,V,N+1) - A(T,V,N), \tag{9}$$

where A is the Helmholtz free energy. Differentiating A with respect to N may be written as the Helmholtz free-energies difference because of the fact that it is an extensive property, and the addition of one particle to a macroscopic system can be considered to be an infinitesimal change for the variable N. Instead of adding one particle to the system, we insert it at a fixed position, R_0. The change in the Helmoltz free energy for such insertion, μ^*, is given as

$$\begin{aligned}\mu^* &= A(T,V,N+1,R_0) - A(T,V,N)\\ &= -kT\ln\left[\frac{q^{N+1}V^N}{\Lambda^{3N}N!}\right] + kT\ln\left[\frac{q^N V^N}{\Lambda^{3N}N!}\right] = -kT\ln q.\end{aligned} \tag{10}$$

Therefore Eq. 8 may be written as

$$\mu = \mu^* + kT\ln\frac{V}{N}\Lambda^3. \tag{11}$$

Hence, the work required for adding one particle to the system is partly for inserting the particle in a fixed position, μ^*, and partly for making that particle free. When the particle is released from its fixed position, its Helmholtz free energy changes in three ways. First, it gains translational kinetic energy, with its corresponding contribution to μ as $kT\ln\Lambda^3$. Second, the particle wanders throughout the entire volume; the corresponding contribution is $-kT\ln V$. Finally, when the particle is at a fixed position, it is distinguishable from all N indistinguishable particles. Therefore, the contribution for such indistinguishability in the chemical potential is $kT\ln N$. The summation of these three contributions is given as $kT\ln\rho\Lambda^3$ in Eq. 11, where $\rho\Lambda^3 < 1$; hence, the contribution of $kT\ln\rho\Lambda^3$ to the chemical potential is always negative.[6]

We now extend this approach to obtain the chemical potential in a dense system, in which intermolecular interactions are present. Just as for Eq. 9, it is possible to write the chemical potential in terms of the free-energy differences as

$$\begin{aligned}\exp(-\beta\mu) &= \exp[-\beta[A(T,V,N+1) - A(T,V,N)]] = \frac{Q(T,V,N+1)}{Q(T,V,N)}\\ &= \frac{q^{N+1}/\Lambda^{3(N+1)}(N+1)!\int\dots\int \mathrm{d}R_0\mathrm{d}R_1\dots\mathrm{d}R_N\exp(-\beta U_{N+1})}{q^N/\Lambda^{3N}N!\int\dots\int \mathrm{d}R_1\dots\mathrm{d}R_N\exp(-\beta U_N)}.\end{aligned} \tag{12}$$

Note that the added particle is denoted by a zero subscript. In order to obtain the chemical potential, we should know U_{N+1} and U_N, the configurational potential energy for a system with N+1 and N particles at fixed temperature and density. Using the assumption of pairwise additivity, the total potential is

$$U_{N+1} = U_N + \sum_{j=1}^{N} U(R_0,R_j). \tag{13}$$

where we consider all interactions between the zeroth particle and the remaining molecules in the last term. Also, we assume that adding this particle does not have any effect on the interactions among the other particles, U_N. Substitution of Eq. 13 in Eq. 12 and assuming that the entire volume is accessible for the zeroth particle (the occupied volume by the particles is taken as zero) we have

$$\exp(-\beta\mu) = \frac{qV}{(N+1)\Lambda^3}\left\langle \exp\left(-\beta\sum_{j=1}^{N}U(R_0,R_j)\right)\right\rangle, \tag{14}$$

where $\langle\exp[-\beta\sum U(R_0,R_j)]\rangle$ is the average of the exponential of $-\beta\sum U(R_0,R_j)$ over the original N-particle system. Assuming that $\rho = N/V = (N+1)/V$, and rearranging of Eq. 14 gives the chemical potential as

$$\mu = kT\ln\rho\Lambda^3 q^{-1} - kT\ln\left\langle \exp\left(-\beta\sum_{j=1}^{N}U(R_0,R_j)\right)\right\rangle. \tag{15}$$

The first term on the right-hand side of Eq. 15 is simply the ideal-gas chemical potential at the same temperature and density. The second term is due to the non-ideal behavior which arises from interactions among the added particle with N particles in the system, which is an unknown quantity in Eq. 15. In this way, the only difference between the chemical potentials of the ideal system and a real system is due to the interactions among the particles in the real system. This means that the non-zero volume of the real particles has been neglected. However, in order to obtain such a chemical potential by Eq. 15, we should know the N-particle configurational potential. Even if we know such a potential, we must assume the pairwise additivity approximation for the potential, and also assume that the addition of one particle to the system does not effect the interactions among the N particles in the system. None of these assumptions is true; moreover, we do not know the exact form of the pair potential in dense systems, which is quite different from the isolated potential.[7] Because of such difficulties in calculating this term in Eq. 15, we try to derive the chemical potential from the exact definition given in Eq. 7 by means of

$$\frac{\mu}{kT} = -\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V} = \ln q^{-1} N \Lambda^{3} - \left(\frac{\partial \ln Z}{\partial N}\right)_{T,V}, \tag{16}$$

where

$$Z = \int \dots \int \exp(-\beta U_N) \mathrm{d}R_1 \dots \mathrm{d}R_N.$$

In this way, if we know the configurational partition function, Z, in terms of known thermodynamic variables, such as V, T, and N, we can obtain the chemical potential using Eq. 16. In this article we should try to obtain this term by using an appropriate equation of state. We select the LIR equation of state, which is suitable for different dense fluids, including polar, non-polar, and hydrogen bonded systems; also, the temperature and composition dependencies of its parameters are known. The partition function is related to the equation of state via

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \tag{17}$$

or

$$\int \mathrm{d}\ln Q = \int \frac{p}{kT}\mathrm{d}V.$$

Using the LIR

$$\ln Q = N\left(\ln V - \frac{A}{2v^2} - \frac{B}{4v^4}\right) + F(T,N), \tag{18}$$

where v is the molar volume and $F(T,N)$ is the constant of integration, which may be obtained by comparing Eq. 18 with Eq. 6 as

$$F(T,N) = N\ln q - \ln N! - N\ln \Lambda^{3}. \tag{19}$$

Substituting Eq. 19 in Eq. 18 and using Eq. 7, we obtain the chemical potential for a dense fluid as

$$\mu = RT\ln \rho \Lambda^{3} q^{-1} + RT\left(\frac{3A}{2}\rho^{2} + \frac{5B}{4}\rho^{4}\right). \tag{20}$$

It is clear from Eq. 20 that the first term in this equation is the chemical potential for an ideal gas, and the second term is related to the non-ideal contributions. Comparing Eq. 15 with Eq. 20 suggests that the contribution of all non-ideality, which is caused by interactions among the zeroth particle and other particles of the system and the effect of a non-zero volume of the particles, may be written as

$$RT\left(\frac{3A}{2}\rho^{2} + \frac{5B}{4}\rho^{4}\right)$$

or

$$\left(\frac{3A''RT}{2}\rho^{2} - \frac{3A'}{2}\rho^{2} + \frac{5B'}{4}\rho^{4}\right). \tag{21}$$

It is remarkable that none of the mentioned approximations used to derive the chemical potential by Eq. 15 appears in this approach given by Eq. 20. In other words, we have obtained a more accurate expression for the chemical potential, in which all contributions for the interactions are considered; additionally, we have taken the effect of the non-zero volume of the particles into account. The quantity in Eq. 21 is referred to as the total binding energy of the added particle with all other particles and the effect of the non-ideal situation caused by the excluded volume in the real system. The non-ideal effect has three contributions, which may be interpreted by using the LIR as the equation of state. The first contribution, $3/2RTA''\rho^2$, which is positive, is due to the covolume of the particles. The other two contributions, $-3/2A'\rho^2$ and $5/4B'\rho^4$, are due to the average contribution of the attractive and repulsive terms, respectively. Because the attraction between the added particle and the other particles in the system causes stability for the particle, its contribution to the chemical potential is negative, while the contribution of the average repulsion is positive.

It is to be noted that although derivation of the non-ideal effect in the chemical potential can be made with any equation of state, using the LIR enables us to give a proper physical interpretation for each contribution.

Chemical Potential of a Component in a Binary Mixture

The chemical potential in the mixed state can be obtained by a straightforward generalization of Eq. 20. For a binary mixture containing N_1 molecules of component 1 and N_2 molecules of component 2, the partition function is given by the LIR as

$$\ln Q = (N_1 + N_2)\left[\ln V - \frac{A(N_1+N_2)^2}{2V^2} - \frac{B(N_1+N_2)^4}{4V^4}\right] - \ln N_1! - \ln N_2!$$
$$-N_1\ln \Lambda_1^{3} - N_2 \ln \Lambda_2^{3} + N_1 \ln q_1 + N_2 \ln q_2, \tag{22}$$

where Λ_2 and q_2 are the momentum and the internal partition function of component 2. We take the differentiation of the Eq. 22 with respect to N_1 at fixed T, V, and N_2 (note that parameters A and B in Eq. 22 depend on the intermolecular interactions and non-ideal thermal pressure and vary with N_1). Thus, by using Eq. 7, we obtain the chemical potential of component 1, μ_1, in the binary mixture as

$$\mu_1 = RT\ln \rho_{\mathrm{mix}} \Lambda_1^{3} q_1^{-1} + \frac{RT}{2v_{\mathrm{mix}}^{2}}(A' - A) + \frac{RT}{4v_{\mathrm{mix}}^{4}}(B' + 3B) + RT\ln x_1, \tag{23}$$

where x_1 is the mole fraction of component 1 in the binary mixture; $v_{\mathrm{mix}} = 1/\rho_{\mathrm{mix}}$ is the molar volume of the mixture, and A', A, B', and B are as follows:

$$\begin{aligned} A' = {} & \left[2x_1\left(\frac{A}{B}\right)_{11} + (2-2x_1)\left(\frac{A}{B}\right)_{11}\right] \\ & \left[x_1^2 B_{11} + (2x_1 - 2x_1^2)B_{12} + (1 + x_1^2 - 2x_1)B_{22}\right] + \\ & \left[x_1^2\left(\frac{A}{B}\right)_{11} + (2x_1 - 2x_1^2)\left(\frac{A}{B}\right)_{12} + (1 + x_1^2 - 2x_1)\left(\frac{A}{B}\right)_{22}\right] \\ & [2x_1 B_{11} + (2 - 2x_1)B_{12}], \end{aligned}$$

$$A=\left[x_1^2\left(\frac{A}{B}\right)_{11}+(2x_1-2x_1^2)\left(\frac{A}{B}\right)_{12}+(1+x_1^2-2x_1)\left(\frac{A}{B}\right)_{22}\right]$$
$$\times\left[x_1^2B_{11}+(2x_1-2x_1^2)B_{12}+(1+x_1^2-2x_1)B_{22}\right],$$
$$B'=[2x_1B_{11}+(2-2x_1)B_{12}],$$

and

$$B=[x_1^2B_{11}+(2x_1-2x_1^2)B_{12}+(1+x_1^2-2x_1)B_{22}]. \tag{24}$$

Comparing Eqs. 23 and 20 suggests that the difference between the first terms of these two chemical potentials is due to the volume within the particle can wander. Therefore, for a particle in a mixture, such a volume depends on concentration, besides the temperature and pressure. The second and third terms in Eq. 23 arise from the intermolecular interactions between a particle of kind 1 in a mixture with mole fraction of x_1 for component 1, in which the covolume of the particles are considered. Finally, the last term is the entropy contribution of random mixing in the chemical potential. It is perhaps more convenient to write Eq. 23 explicitly in terms of T, ρ, x and the LIR parameters as

$$\mu_1=RT\ln\rho\Lambda_1^3q_1^{-1}+RT\ln x$$
$$+\begin{pmatrix} ax^4+bx^3+(c_1+c_2\rho^2/2)x^2+(d_1+d_2\rho^2/2)x \\ +(e_1+e_2\rho^2/2) \end{pmatrix}\rho^2/2, \tag{25}$$

where $x_1\equiv x$ and $\rho\equiv\rho_{\text{mix}}$, and

$$a=-A_{11}-A_{22}-4A_{12}+2\left(\frac{A}{B}\right)_{11}B_{12}+\left(\frac{A}{B}\right)_{11}B_{22}$$
$$+2\left(\frac{A}{B}\right)_{12}B_{11}-2\left(\frac{A}{B}\right)_{12}B_{22}$$
$$-2\left(\frac{A}{B}\right)_{22}B_{11}+2\left(\frac{A}{B}\right)_{22}B_{12},$$
$$b=-8\left(\frac{A}{B}\right)_{11}B_{12}+4\left(\frac{A}{B}\right)_{11}B_{22}-8\left(\frac{A}{B}\right)_{12}B_{11}$$
$$-8\left(\frac{A}{B}\right)_{12}B_{22}-8\left(\frac{A}{B}\right)_{22}B_{12}+4\left(\frac{A}{B}\right)_{22}B_{11}$$
$$+4A_{11}+4A_{22}+16A_{12},$$
$$c_1=-5\left(\frac{A}{B}\right)_{11}B_{22}+12\left(\frac{A}{B}\right)_{12}B_{22}-5\left(\frac{A}{B}\right)_{22}B_{11}$$
$$+12\left(\frac{A}{B}\right)_{22}B_{12}+6\left(\frac{A}{B}\right)_{11}B_{12}+6\left(\frac{A}{B}\right)_{12}B_{11}$$
$$-20A_{12}-6A_{22},$$
$$c_2=3B_{11}-6B_{12}+3B_{22}$$
$$d_1=-8\left(\frac{A}{B}\right)_{12}B_{22}-8\left(\frac{A}{B}\right)_{22}B_{12}+2\left(\frac{A}{B}\right)_{11}B_{22}$$
$$+2\left(\frac{A}{B}\right)_{22}B_{11}+4A_{22}+8A_{12},$$
$$d_2=2B_{11}+4B_{12}-6B_{22},$$
$$e_1=2\left(\frac{A}{B}\right)_{12}B_{22}+2\left(\frac{A}{B}\right)_{22}B_{12}-A_{22},$$
$$e_2=3B_{22}+2B_{12}. \tag{26}$$

Equation 25 shows that the chemical potential of component 1 in a binary mixture, in addition to $RT\ln x$, has a function of mole fraction, which is quartic and arises from the intermolecular interactions and molecular covolumes.

It has been clarified that the derived chemical potential is valid for the entire range of compositions, from $x=0$ to $x=1$. Therefore, it should satisfy Henry's law in the limit of $x\rightarrow0$. When x approaches zero, the quartic terms of x become negligible in comparison to $RT\ln x$, except for $(e_1+e_2\rho^2/2)\rho^2/2$. We then have,

$$\mu_1=RT\ln\rho\Lambda^3q^{-1}+(e_1+e_2\rho^2/2)\rho^2/2+RT\ln x,$$
$$\mu_1=\mu^\circ+RT\ln x, \tag{27}$$

where μ^0 is the reference chemical potential for the solute according to Convention II.[8] It is also remarkable to show that Eq. 25 satisfies Raoult's law in the limit $x\rightarrow1$. In this limit, ρ_{mix} approaches to the pure-solvent density and $A'\rightarrow4A$, $B'\rightarrow3B$. Therefore, Eq. 23 reduces to

$$\mu_1=RT\ln\rho\Lambda^3q^{-1}+3/2A\rho^2+5/4B\rho^4+RT\ln x,$$

or

$$\mu_1=\mu^\theta+RT\ln x, \tag{28}$$

where μ^θ is the chemical potential of a pure solvent. Equation 28 is Raoult's law.

In order to check the accuracy of the obtained chemical potential with that reported in the literature, there are two difficulties. First, the internal partition function (q) should be known, which is a difficult task. Second, the reported chemical potential in the literature depends on an arbitrary reference state. We shall therefore examine the obtained chemical potential via a solubility prediction, which is a sever test.

Solubility Prediction via the Chemical Potential

Consider two phases, α and β, in which N_i molecules of component i are distributed. For equilibrium between two phases at the same temperature and pressure, we have

$$\mu_i^\alpha=\mu_i^\beta. \tag{29}$$

We can obtain the equilibrium concentration in a binary mixture via this equality by using the obtained chemical potentials (Eqs. 25 and 20). In addition to the LIR limitations (discussed later), one more assumption is the applicability of classical statistical mechanics. As a first attempt, we examined the solubility of NH_3 in water because of the nearly same intermolecular interactions. To simplify the system as a binary mixture, we ignored the ionic dissociation of NH_3 because of its small dissociation constant. The μ_{NH_3} in solution is calculated from Eq. 25, and the other phase may be treated as a pure phase, for which the ammonium chemical potential is obtained from Eq. 20. Because of the fact that the values of these two chemical potentials at any equilibrium concentration at fixed temperature and pressure must be equal, we dropped the term $kT\ln q^{-1}$ from both sides of the equality. In other words, we calculated $\mu-\mu^*$ for NH_3 in pure and mixed states. We first calculated the chemical potential of NH_3 in the solution using the experimental values of the mole fraction[9] at any given temperature and pressure and the LIR parameters, which have been calculated using p-v-T data taken from Refs. 10 and 11. The density of the pure and mixed states were also calculated from the LIR equation of state. The calculated values of $(\mu-\mu^*)/RT$ for NH_3 in the pure and mixed states are summarized in Table 1. If our treatment were exact, the calculated chemical potential of NH_3 in two phases at equilibrium would be equal. However, the values of these two chemical potentials are not exactly the same. These discrepancies may be attributed to the following limitations:

1. The LIR mixing rule is based on random mixing, or considering a regular solution. This assumption is accurate at high temperatures for components with approximately similar interactions. This assumption is therefore not valid for systems with partial miscibility, owing to the fact that the solute molecules do not distribute randomly among the solvent molecules when the interactions are significantly different. This mixing rule may simply be regarded as only an approximation.

2. The unlike interactions, $(A/B)_{12}$ and B_{12}, are assumed to be the mean geometric of those values for the pure components. The mean geometric approximation is valid mostly for components with similar intermolecular interactions.[5] However, we have used it as an approximation; in some cases we must consider an adjustable parameter.

3. In our approach the contribution of internal degrees of freedom in the chemical potential, $kT\ln q^{-1}$, is taken to be equal in the pure and mixed states. This means that the solvent molecules have no effect on the internal degrees of freedom of the solute. This is also an approximation that fails for large solute molecules, such as polymers.

Therefore, we may expect that the obtained chemical potentials of NH_3 in the pure and mixed states are not exactly the same due to using the above-mentioned approximation. In spite of such limitations, we have used the equality of the derived expression for the chemical potentials, Eqs. 20 and 25, to predict the solubility.

In order to predict the solubility of NH_3 in H_2O in any thermodynamic state, we set $\mu-\mu^*$ by using Eq. 20 for the pure phase equal to $\mu-\mu^*$, obtained from Eq. 25 for the mixed state. Since all coefficients and densities needed to calculate chemical potentials can be obtained from the LIR in any thermodynamic state, we can obtain the equilibrium mole fraction at that temperature and pressure. The values of a, b, c_1, c_2, d_1, d_2, e_1, and e_2 of Eq. 25 are summarized in Table 2 for some given isotherms. The calculated mole fraction by this approach is compared with the experimental values in Table 3. The results of the solubility show that the agreement between the experimental and calculated values improves with increasing pressure. This agreement is very remarkable because we have not used any adjustable parameter for the chemical potential. However, in order to improve the results, an adjustable parameter may be introduced.

Table 1. Chemical Potential and Density of NH_3 in the Pure $(\rho_p,(\mu-\mu^*)_p)$ and Mixed $(\rho_m,(\mu-\mu^*)_m)$ States at Given Thermodynamic States. The Experimental Solubility, $x(NH_3)$, Has Been Cited

$x(NH_3)$	$\rho_m/\mathrm{mol\,l^{-1}}$	$\rho_p/\mathrm{mol\,l^{-1}}$	T/K	$(\mu-\mu^*)_p/RT$	$(\mu-\mu^*)_m/RT$
0.5168	46.6662	36.5037	273.1500	−11.2013	−12.3296
0.5238	46.5248	36.5039		−11.2012	−12.2982
0.5474	46.0524	36.5048		−11.2009	−12.1974
0.6121	44.7396	36.5060		−11.2005	−11.9538
0.6277	44.4211	36.5064		−11.2004	−11.9016
0.6508	43.9472	36.5073		−11.2001	−11.8287
0.6571	43.8162	36.5076		−11.2000	−11.8098
0.6662	43.6296	36.5082		−11.1998	−11.7827
0.3489	49.3423	35.0648	293.1500	−11.0435	−13.0274
0.3651	49.0121	35.0651		−11.0434	−12.9203
0.4208	47.8692	35.0665		−11.0430	−12.5843
0.4239	47.8055	35.0662		−11.0431	−12.5660
0.4309	47.6615	35.0668		−11.0429	−12.5280
0.4373	47.5272	35.0671		−11.0428	−12.4933
0.4819	46.5991	35.0671		−11.0428	−12.2679
0.4994	46.2314	35.0698		−11.0421	−12.1860
0.5394	45.3870	35.0727		−11.0412	−12.0147
0.5597	44.9562	35.0744		−11.0407	−11.9348
0.5692	44.7531	35.0752		−11.0405	−11.8990
0.2501	50.7954	33.8513	310.1500	−10.9434	−13.6019
0.2537	50.7225	33.8515		−10.9434	−13.5716
0.3069	49.6292	33.8532		−10.9430	−13.1470
0.3268	49.2174	33.8542		−10.9427	−13.0026
0.3313	49.1218	33.8544		−10.9427	−12.9713
0.3633	48.4519	33.8564		−10.9422	−12.7591
0.3903	47.8815	33.8582		−10.9418	−12.5929
0.4113	47.4344	33.8592		−10.9415	−12.4709
0.4293	47.0515	33.8615		−10.9410	−12.3728
0.4662	46.6861	33.8635		−10.9405	−12.2845

Table 2. The Parameters of Chemical Potential Equation, Eq. 25, for Solubility of NH_3 in H_2O for Given Isotherms, Calculated from the LIR Parameters and Eq. 26

T/K	273.15	293.15	310.15
A	5.8e−3	5.6e−3	5.4e−3
b	−2.0e−3	−2.1e−3	−2.3e−3
c_1	6.4e−3	6.5e−3	6.6e−3
c_2 (l^2mol^{-2})	3.591e−6	3.456e−6	3.373e−6
d_1	−9.4e−3	−8.5e−3	−7.8e−3
d_2 (l^2mol^{-2})	1.0412e−5	1.0449e−5	9.9536e−6
e_1	−0.0139	−0.0135	−0.0131
e_2 (l^2mol^{-2})	6.1982e−6	6.1315e−6	6.0524e−6

Table 3. The Experimental, x_{exp}, and Calculated Solubility, x_{cal}, of NH_3 in H_2O for Several Thermodynamic States

T/K	p/atm	$x_{exp}(NH_3)$	$x_{cal}(NH_3)$
273.15	1.2039	0.5168	0.5600
	1.2421	0.5238	0.5600
	1.5000	0.5474	0.5800
	1.8539	0.6121	0.6100
	1.9737	0.6277	0.6200
	2.2158	0.6508	0.6400
	2.2789	0.6571	0.6400
	2.4539	0.6662	0.6500
293.15	0.9697	0.3489	0.4400
	1.0618	0.3651	0.4600
	1.5105	0.4208	0.4900
	1.5434	0.4239	0.5000
	1.6237	0.4309	0.5040
	1.6961	0.4373	0.5080
	2.2158	0.4819	0.5340
	2.5579	0.4994	0.5400
	3.5000	0.5394	0.5700
	4.0520	0.5597	0.5800
	4.3171	0.5669	0.5900
310.15	1.0368	0.2501	0.3900
	1.0658	0.2537	0.3900
	1.5342	0.3069	0.4300
	1.7947	0.3268	0.4400
	1.8487	0.3313	0.4400
	2.3829	0.3633	0.4600
	2.8974	0.3903	0.4800
	3.2618	0.4113	0.4900
	3.7500	0.4293	0.5000
	4.2682	0.4462	0.5100

We may conclude that when the intermolecular interactions and molecular sizes of the solvent and solute are nearly the same, the random mixing and the mean geometric approximations become more reasonable. Therefore, our approach in predicting the solubility becomes more accurate. Also, the assumption concerning the identity of the contribution of the internal degrees of freedom in the chemical potential in both phases becomes more realistic. Therefore, when the solubility is large, for which the solvent and solute molecules are similar, our approach without including any adjustable parameter can be used to predict the solubility.

However, it is desirable to predict the solubility when the miscibility is not too large and the intermolecular interactions and molecular sizes are significantly different. In such cases, we can't predict the solubility by using the LIR mixing rule. Also, the assumption of a mean geometric for unlike interactions doesn't hold. The deficiency due to these assumptions, namely, the random mixing, mean geometric, and identity of the internal degrees of freedom in both phases, are simply considered as an adjustable parameter for the unlike interactions in the LIR parameters (A_{12}, B_{12}, and $(A/B)_{12}$). An example for such a case is the solubility of gaseous CO_2 in liquid benzene with different molecular sizes. Note that the density of this solution is in the range of the applicability of the LIR. We have used Eq. 25 to calculate the chemical potential of CO_2 in solution (the p-v-T data for obtaining the LIR parameters is taken from Refs. 12 and 13). However, for the pure gas phase, CO_2, which is in equilibrium with the solution, the LIR equation of state, can't be used because of the low density. Therefore, we have used the virial equation of state as an appropriate equation of state for the low densities, and truncate it after the third term. In a similar way to that used by taking the LIR, the chemical potential of the pure component may be derived as

$$\frac{\mu}{RT} = \ln \rho \Lambda^3 q^{-1} + \frac{B}{v} + \frac{C}{2v^2}, \tag{30}$$

where B and C are the second and third virial coefficients. The chemical potential for the pure phase of CO_2 has been calculated from Eq. 30 (the virial coefficients are taken from Ref. 14) and for the mixed state from Eq. 25. These two values are found to be quite different for the 303.15 K isotherm (Table 4). Therefore, we obtained an adjustable parameter for the unlike interactions to satisfy the condition of the equality of these two chemical potentials at equilibrium. The adjustable parameter for the equality of the chemical potentials of CO_2 at 303.15 K was found to be 0.7872 from a least-squares fitting. We then used this adjustable parameter for

Table 4. The Chemical Potential of CO_2 in the Pure Phase, $(\mu-\mu^*)_p$, and in the Solution, $(\mu-\mu^*)_m$ Calculated from the Virial and LIR Equations of State Respectively at 303.15 K. The Densities of the Pure State, ρ_p, and Mixed State, ρ_m, Are Given

$x_{exp}(CO_2)$	ρ_m/mol l^{-1}	ρ_p/mol l^{-1}	$(\mu-\mu^*)_m/RT$	$(\mu-\mu^*)_p/RT$
0.1310	12.9100	0.4610	−31.2602	−13.9061
0.1720	13.4400	0.6110	−30.0916	−13.6408
0.2130	13.9700	0.7768	−28.7804	−13.4188
0.2550	14.5000	0.9342	−27.3187	−13.2514
0.3000	15.0700	1.1351	−25.6211	−13.0783
0.3420	15.6100	1.2800	−23.9293	−12.9737
0.4030	16.3800	1.6567	−21.4270	−12.7559
0.4800	17.2400	1.9498	−18.6259	−12.6238
0.5340	18.0100	2.1773	−16.3455	−12.5373
0.5450	18.1500	2.2278	−15.9522	−12.5196
0.5850	18.6400	2.3920	−14.6621	−12.4655
0.6220	19.0900	2.5496	−13.6128	−12.4180
0.6540	19.4700	2.5840	−12.8466	−12.4081
0.8080	21.2000	3.3990	−10.9470	−12.2167
0.8400	21.5000	3.7653	−10.9204	−12.1508
0.8820	21.8100	4.1798	−11.0292	−12.0871

the unlike interactions in Eq. 25 to predict the solubility for the 303.15 K isotherm. The predicted solubility is compared with the experimental data[9] in Fig. 1. As can be clearly seen, the discrepancy takes place at high pressures, which is expected to be due to a limitation of the internal motions of CO_2 molecules when they are surrounded by solvent molecules. The internal motions of a confined CO_2 molecule in a solvent cage is quite limited compared to that molecule in the gas phase. As mentioned before, this adjustable parameter is introduced to compensate for any deficiency arising from the three mentioned limitations. However, a single adjustable parameter is not sufficient for the entire pressure range when the third limitation is fundamentally different in two phases, like CO_2 in the pure gas phase and a dense liquid solution. This difference between the internal degrees of freedom in two phases varies with the pressure and becomes more significant at high pressures. We have also used this adjustable parameter to predict the solubility for other isotherms of CO_2 in C_6H_6. We have shown the predicted solubility by using the LIR parameters, virial coefficients, and the adjustable parameter found from the equality of the chemical potentials for the 303.15 K isotherm in Figs. 2a and 2b. The agreement between the experimental and calculated values is similar to those obtained for the 303.15 K isotherm. By using the experimental values of the solubility just for an isotherm we are able to predict the solubility at any desirable state for which experimental data are not available.

We have also predicted the solubility of C_6H_6 in N_2[9] with an adjustable parameter, found to be −0.8605. The p-v-T data needed to determine the LIR parameters was taken from Jacobsen et al.[15] The agreement between the experimental and calculated values of solubility with such an adjustable parameter is superior (Table 5). Because of the LIR density limitation, we have not predicted the solubility in this system for other reported states for which the density is lower than the Boyle density.

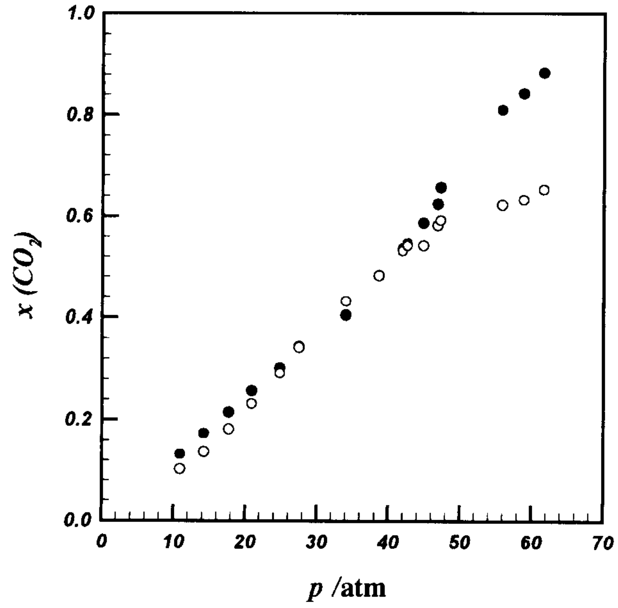

Fig. 1. The calculated solubility (○) of CO_2 in C_6H_6 vs. pressure compared to the experimental values (●) for 303.15 K isotherm.

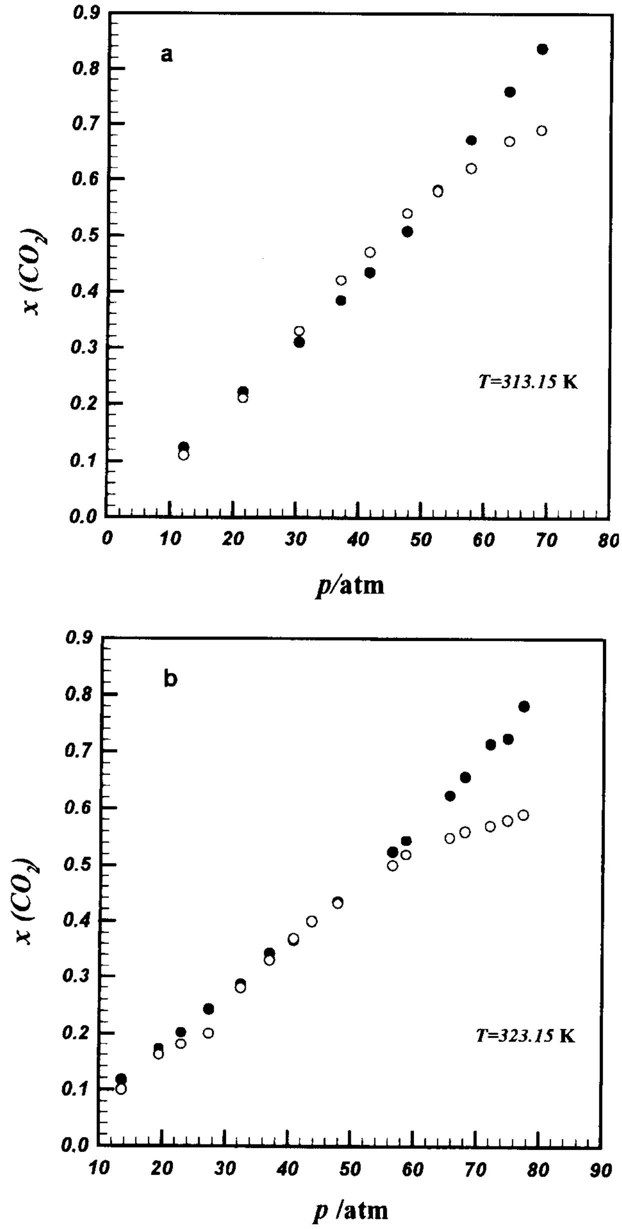

Fig. 2. Solubility predicting of CO_2 in C_6H_6 vs. pressure using the obtained adjustable parameter (0.7827) from 303.15 K isotherm for (a) 313.15 K and (b) 323.15 K.

Table 5. The Experimental, x_{exp}, and Calculated, x_{cal}, Solubility of N_2 in C_6H_6 in Several Given Thermodynamic States

t/°C	p/atm[a)]	ρ_p/mol l^{-1}	ρ_m/mol l^{-1}	$x_{exp}(N_2)$	$x_{cal}(N_2)$
15.0	1000	19.8600	12.1300	.0155	.0162
15.0	1100	20.4800	12.1900	.0158	.0170
30.0	1000	18.7500	12.0200	.0213	.0210
30.0	1100	19.3400	12.0800	.0218	.0219

a) 1 atm = 101325 Pa.

Conclusion

In this article we have derived an expression for calculating the chemical potential of a component in both the pure and mixed states using the LIR and statistical thermodynamics. Using the LIR, we have been able to interpret all of the terms that appear in the chemical-potential expression. In fact, we derived the contribution of the non-ideality in three parts. First, the average effective attraction, $-3/2A'\rho^2$, which has a negative contribution to the chemical potential; second, the average effective repulsion contribution, $5/4B'\rho^4$, with a positive contribution; and finally, the contribution due to the non-zero volume of particles, $3/2A''RT\rho^2$, in the chemical potential. The separation of these three contributions to the chemical potential for real systems in this interesting way is possible by using only the LIR.

As we know, predicting solubility is a sever test for the mixture equation of sate. The results of this work indicate that the LIR is a strong regularity which is successful in predicting of the solubility, at least when the molecules of the solvent and the solute are similar, without any adjustable parameters. From the fact that this regularity is applicable for different dense fluid systems, such as polar, non-polar, and hydrogen-bonded systems, we may conclude that our approach along with the LIR can be used for all different dense fluids. Since the temperature dependencies of the parameters of the chemical potentials are known in terms of the LIR parameters, we may predict the solubility, even at some temperatures for which experimental data is not available.

In cases where the solvent and solute are not similar, from the view point of the intermolecular interactions and molecular sizes, we may also predict only the solubility by having experimental values of the solubility for an isotherm. From these we can obtain the value of the adjustable parameter, and use it for other isotherms for which no experimental data is available. As we shown for CO_2 in C_6H_6, the agreement between the experimental and calculated values for such isotherms is similar to that obtained from a least-squares fitting of the experimental data (compare Fig. 2 with Fig. 1).

Finally, it should be noted that our approach for deriving the chemical potential is general, and is not limited to the LIR. Depending on the system of interest, an appropriate equation of state can be used. For example, for low density we used the virial equation of state. The success of this approach strongly depends on the accuracy of the mixing rule of the equation of state. If the mixing rule is sufficiently accurate we may expect that the solubility can be predicted without any adjustable parameter.

We acknowledge Dr. B. Najafi for his fruitful comments and the Isfahan University of Technology Research Council for its financial support.

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