

Appendix D

Densities of Solutes in Aqueous Mixtures

In this report, the densities of solvents in nonaqueous mixtures are assumed to be the same as their density as pure components. These values of density are then used to compute the amount of each component in a given volume of mixture. For aqueous solutions, however, all components of the mixture are assumed to have a density of 1 g.cc^{-1} . This assumption is made because of the difficulty of determining appropriate values for the densities of solutes on polar solvents such as water. This Appendix describes the relationships between component densities and intermolecular forces in liquid mixtures, and indicates the problems associated with estimation of the density.

The density of a component i in solution at a given mole fraction x_i can be related to a quantity called the partial molar volume, V_i :

$$\rho_i(x_i) = \frac{M_i}{V_i(x_i)}$$

where M_i is the molecular weight of the component. The partial molar volume is defined by:

$$V_i = \left(\frac{\partial V}{\partial n_i} \right)_{n_j}$$

n_i being the number of moles of i and V the volume of one mole of the mixture. V and V_i are also related by:

$$V = \sum x_i V_i$$

which allows us to determine the amount of component i in the mixture once V_i is known.

Now, it is shown in standard texts on thermodynamics (e.g., J.M. Smith and H.C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*) that the partial molar volume V_i is related to the chemical potential μ_i :

$$V_i = \left(\frac{\partial \mu_i}{\partial P} \right)_T$$

and the chemical potential can be divided into two parts, one part representing the chemical potential of i in an ideal mixture (IM), and the other part representing the excess (E) chemical potential due to the interaction of molecules of component i with other components of the solution:

$$\mu_i = \mu_i^{IM} + \mu_i^E$$

Substituting into eq. (4) gives:

$$V_i(x_p, T, P) = V_i(x_i=1, T, P) + \left(\frac{\partial \mu_i^E}{\partial P} \right)_T$$

The first term on the right is simply the molar volume of pure liquid i . The second term can be related to the activity coefficient γ_i of i in solution:

$$V_i(x_p, T, P) = V_i(x_i=1, T, P) + RT \left(\frac{\partial \ln \gamma_i}{\partial P} \right)_T$$

In an ideal solution, such as those formed by mixtures of nonpolar solvents, the activity coefficient of each component is approximately 1 and the pure component molar volume (or density) can be used to find the amount of i in a given volume of the mixture. In polar solvents such as water, the activity coefficients are usually far from 1, especially when the mole fraction of i is small. In this case, we can replace the activity coefficient with the Henry's constant:

$$V_i(x_p, T, P) = V_i(x_i=1, T, P) + RT \left(\frac{\partial \ln(H_i/P_i^{sat})}{\partial P} \right)_T$$

where P_i^{sat} is the saturation vapor pressure of i at the temperature of interest. Henry's constants are generally assumed to be independent of pressure, making evaluation of the derivative impossible. Alternatively, we can use an activity coefficient correlation such as the Wilson equation, which is generally valid for homogenous mixtures:

$$\ln \gamma_i = 1 - \ln(\sum_j x_j G_{ij}) - \sum_k \left(\frac{x_k G_{ki}}{\sum_j x_j G_{kj}} \right)$$

where

$$G_{ij} = \frac{V_j(x_j=1)}{V_i(x_i=1)} \exp\left(\frac{-a_{ij}}{RT}\right)$$

the a_{ij} terms being related to the energy of interaction of components i and j . In principle, the effect of pressure on the activity coefficients can be taken into account by using the isothermal compressibility β

$$\beta = \frac{1}{V} \frac{\partial V}{\partial P}$$

to alter the pure-component molar volumes in eq. (10). However, the Wilson equation, and most other activity coefficient correlations in current use, are derived from rigid-lattice models that do not account for pressure effects. Therefore, partial molar volumes derived on this basis are not likely to be correct. In a liquid, changes in external pressure result in changes in the radial distribution function $g(r)$:

$$\frac{P}{kT} = \frac{N}{V} - \frac{1}{6kT} \left(\frac{N}{V}\right)^2 \int_0^\infty \frac{\partial u(r)}{\partial r} g(r) 4\pi r^3 dr$$

where $u(r)$ is the energy of two molecules separated by a distance r and $g(r)$ is the probability of finding two particles separated by that distance (L.E. Reichl, *A Modern Course in Statistical Physics*).

Increasing pressure will cause the molecules to assume more and more energetically unfavorable configurations, both by moving closer together and by twisting internally and externally. The chemical potential of solute i is the work associated with bringing a molecule of i into the solution from an infinite distance away (this is similar to the definition of electrostatic potential). This can be mathematically represented by "hiding" the molecule's force field from the surrounding liquid and then slowly making it visible, using a factor λ that is varied from 0 to 1:

$$u_i(r)_{\text{apparent}} = \lambda u_i(r)$$

The chemical potential is then:

$$\mu_i = \mu_i^{\text{Ideal Gas}} - \frac{N}{V} \int_0^1 \int_0^\infty u_i(r) g_i(r, \lambda) 4\pi r^3 dr d\lambda$$

Since water and most solutes of interest are not spherically symmetric, use of this equation requires a series of molecular mechanics simulations over the range $\lambda = 0 \rightarrow 1$. In practice, it is found that for $\lambda = 0 \rightarrow 0.25$, the solute molecule hardly interacts with the solvent at all and drifts through it like a particle in a slightly nonideal gas. A relatively simple angle-averaged calculation gives the contribution to the chemical potential in this region. However, at least one or two simulations must still be performed at or near $\lambda = 1$ with the complete molecular geometry taken into account. At present, these types of calculations are too compute-intensive to run on personal computers and must be run on workstations or mainframes. Such simulations are used fairly widely in the pharmaceutical industry to study the behavior of new drugs, but they are not yet routinely used to predict physical properties for engineering purposes.

In addition to the issues noted above, two other problems arise in dealing with many aqueous solutions. The first is that, in the case of weakly dissociating compounds such as acetic acid, it is difficult to know what the mole fraction of each component in solution actually is. The second problem is that, in the case of salts such as sodium chloride, one would need

to know the molar volume of pure liquid NaCl ($V_1(x_1=1, T, P)$). However, sodium chloride is a solid below 804 °C and the properties of the hypothetical liquid state are not available.