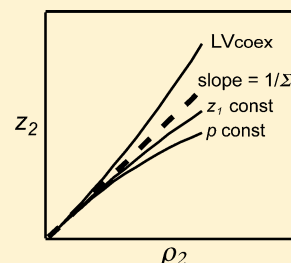


Second Osmotic Virial Coefficient from the Two-Component van der Waals Equation of State

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ABSTRACT: The second osmotic virial coefficient is in principle obtained from the second-order term in the expansion of the osmotic pressure Π or solute activity z_2 in powers of the solute density ρ_2 at fixed solvent activity z_1 and temperature T . It is remarked that the second-order terms in the analogous expansions at fixed pressure p or at liquid–vapor coexistence instead of at fixed z_1 also provide measures of the effective, solvent-mediated solute–solute interactions, but these are different measures. It is shown here how the function $z_2(\rho_2, z_1, T)$ required to obtain the second osmotic virial coefficient B from an expansion in ρ_2 may be obtained from an equation of state of the form $p = p(\rho_1, \rho_2, T)$ with ρ_1 the solvent density, and also how the analogous coefficient B' in the fixed- p expansion may be so obtained. The magnitude of the difference $B - B'$ is often much smaller than that of B and B' separately, so B' is sometimes an acceptable approximation to B . That is not true of the analogous coefficient in the expansion at liquid–vapor coexistence. These calculations are illustrated with the van der Waals two-component equation of state and applied to solutions of propane in water as an example.



1. INTRODUCTION

The second osmotic virial coefficient in a dilute solution of a solute in a solvent is a measure of the solvent-mediated solute–solute interactions. It measures the leading deviation from the ideal-dilute limit and as such is the analogue of the second virial coefficient in a dilute gas. Like the latter, it is negative when the effective interactions are dominantly attractive and positive when they are dominantly repulsive. It may also be correlated with the solubility: the lower the solubility, the more negative the virial coefficient.¹

In a two-component liquid mixture in which the activity of the solvent (component 1) is z_1 and that of the solute (component 2) is z_2 , the pressure p as a function $p(z_1, z_2, T)$ of those variables and of the temperature T is a thermodynamic potential (that of the grand-canonical ensemble in statistical mechanics). The osmotic pressure Π is the difference between this pressure and the pressure $p(z_1, 0, T)$ of the pure solvent at the same activity z_1 and temperature T

$$\Pi \equiv p(z_1, z_2, T) - p(z_1, 0, T) \quad (1)$$

The activities z_i are here taken to be related to the conventionally defined chemical potentials μ_i by

$$z_i = \frac{1}{\Lambda_i^3} e^{\mu_i/kT} \quad (2)$$

with Λ_i the thermal de Broglie wavelength of the species i and k the Boltzmann constant. They have thus been normalized to become equal to the respective number densities ρ_i in an ideal gas

$$z_i = \rho_i e^{[\mu_i - \mu_i(\text{i.g.})]/kT} \quad (3)$$

where $\mu_i(\text{i.g.})$ is the chemical potential of species i when it is at density ρ_i in a hypothetical ideal gas at temperature T . The Λ_i

occur in μ_i and $\mu_i(\text{i.g.})$ only by arbitrary convention. They cancel in both (2) and (3) and are not present in the z_i .

In the limit of infinite dilution of the solute in the solvent (the ideal-dilute limit), the solute activity becomes proportional to its number density (Henry's law)

$$z_2 \sim \rho_2 / \Sigma \quad (\rho_2 \rightarrow 0) \quad (4)$$

where Σ will here be called the solubility of the solute in the solvent. It is a dimensionless quantity closely related to the conventionally defined Henry's-law constant and to the Ostwald absorption coefficient. If the vapor in equilibrium with the liquid solution were an ideal gas, Σ would then be the ratio of the number density of the solute in the solution to that in the vapor, which is the Ostwald coefficient. It is a fundamental property of the solute–solvent interaction and may be obtained in statistical mechanics from the potential-distribution theorem

$$\Sigma = \langle e^{-\Psi/kT} \rangle \quad (5)$$

where Ψ is the energy of interaction of a test-particle solute molecule inserted into and interacting with the pure solvent and where $\langle \dots \rangle$ denotes a canonical average with the Boltzmann weight that of the solvent.

In the ideal-dilute limit, the osmotic pressure Π is given by van 't Hoff's law

$$\Pi \sim \rho_2 kT \quad (\rho_2 \rightarrow 0) \quad (6)$$

The second osmotic virial coefficient determines the beginning of the deviations of Π and z_2 from their ideal-dilute limits (4)

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and (6) when they are expanded in powers of ρ_2 at fixed z_1 and T

$$\Pi = \rho_2 kT(1 + B\rho_2 + \dots) \quad (\text{fixed } z_1, T) \quad (7)$$

$$z_2 = \frac{1}{\Sigma} \rho_2(1 + 2B\rho_2 + \dots) \quad (\text{fixed } z_1, T) \quad (8)$$

where B is that virial coefficient.

The conditions of fixed z_1 and T in these expansions are essential.^{2,3} It will be seen in section 2 that with other prescribed conditions on the expansion of z_2 in powers of ρ_2 one obtains alternative measures of the solvent-mediated solute–solute interactions responsible for the deviations from the limiting law (4), but it is only the coefficient B in the fixed z_1, T expansions that is related to the integral of the solute–solute pair correlation function $h_{22} = \exp(-w/kT) - 1$ at infinite dilution by

$$B = -\frac{1}{2} \int h_{22} d\tau = -\frac{1}{2} \int [\exp(-w/kT) - 1] d\tau \quad (9)$$

where w is the solute–solute pair potential of mean force at infinite dilution and the integrations are over all space with element of volume $d\tau$.

This, to now, has essentially been a summary of the McMillan–Mayer solution theory.² Equation (9) is also the infinitely dilute limit of one of the Kirkwood–Buff relations.^{4–7}

There are many ways of expressing the deviations from the ideal-dilute limit that result from the effective solute–solute interactions.^{3,8} In section 2, we shall refer to two alternative expansions analogous to (8). In one, the expansion is subject to the condition of fixed T and coexistence of the liquid solution with its vapor, and in the other, the condition is fixed T and pressure p . These share with (8) the leading term ρ_2/Σ but have different coefficients in the term of order ρ_2^2 , i.e., different values of the second derivative $(\partial^2 z_2 / \partial \rho_2^2)^\circ$, where the superscript $^\circ$ means evaluated at $\rho_2 = 0$ (infinite dilution). The second osmotic virial coefficient is uniquely

$$B = \frac{1}{4} \Sigma \left(\frac{\partial^2 z_2}{\partial \rho_2^2} \right)_{T, z_1}^\circ = \frac{1}{2kT} \left(\frac{\partial^2 p}{\partial \rho_2^2} \right)_{T, z_1}^\circ \quad (10)$$

where the second form follows from (1) and (7); or, equivalently,

$$B = -\frac{1}{2kT\Sigma^2} \left(\frac{\partial^2 p}{\partial z_2^2} \right)_{T, z_1}^\circ = -\frac{1}{4\Sigma^2} \left(\frac{\partial^2 \rho_2}{\partial z_2^2} \right)_{T, z_1}^\circ \quad (11)$$

These second derivatives are all at fixed T and z_1 . It will be seen in section 2 that when z_2 is expanded in powers of ρ_2 at fixed T and p instead of fixed T and z_1 the resulting $(\partial^2 z_2 / \partial \rho_2^2)_{T, p}^\circ$ may be an acceptable approximation to $(\partial^2 z_2 / \partial \rho_2^2)_{T, z_1}^\circ$, but the corresponding second derivative at liquid–vapor coexistence and fixed T will not be and is often even opposite in sign to the osmotic B .

Often, from fitting an analytical equation of state to experiment, especially to liquid–vapor equilibrium data, one obtains an expression for the pressure as a function of the densities ρ_1 and ρ_2 instead of the activities z_1 and z_2 . In section 3, it is shown how, schematically, from knowledge of the solution equation of state in the form $p = p(\rho_1, \rho_2, T)$, one may obtain $z_2(\rho_2, z_1, T)$, which is what one needs for the expansion (8) and the subsequent identification of B . In section 4, the

analysis is illustrated with the van der Waals two-component equation of state and applied, as an example, to the solution of propane in water at 25 °C. The concluding section 5 is a summary.

2. THE z_2, ρ_2 PLANE AT FIXED T

In Figure 1 are shown schematically three curves, all at the same fixed T . The one marked LVcoex is the liquid branch of

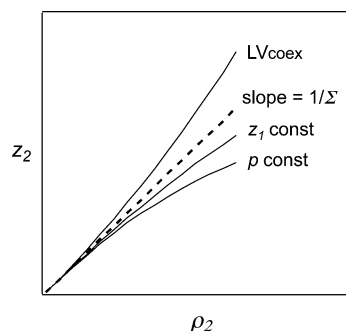


Figure 1. Schematic representation of three curves in the ρ_2, z_2 plane at fixed temperature, all with common slope $1/\Sigma$ at the origin but different curvatures. The curve LVcoex is the liquid branch of the liquid–vapor coexistence curve, and the others are the curves on which either the solvent activity z_1 or the pressure p is held constant.

the liquid–vapor coexistence curve at fixed T , the other two being z_2 as functions of ρ_2 at fixed solvent activity z_1 and at fixed pressure p . Each is a one-dimensional manifold of thermodynamic states with the single degree of freedom that remains in a two-component system when fixed temperature and one additional constraint are imposed. The three curves share a common slope $1/\Sigma$ at the origin but have different limiting second derivatives there. Although these curves are schematic, their relative curvatures are representative of hydrocarbon solutes in water:

$$\begin{aligned} (\partial^2 z_2 / \partial \rho_2^2)_{T, p}^\circ &< (\partial^2 z_2 / \partial \rho_2^2)_{T, z_1}^\circ < 0 \\ &< (\partial^2 z_2 / \partial \rho_2^2)_{T, \text{LVcoex}}^\circ \end{aligned} \quad (12)$$

Each is associated with an expansion of the same form as that in (8), but it is only the expansion at fixed z_1 whose initial curvature yields the second osmotic virial coefficient [the first equality in (10)]. Since the initial slope $1/\Sigma$ is common to all three, their curvatures are all measures, although different measures, of the effective solute–solute interactions that are responsible for the deviations from the ideal-dilute limit.

With the typical analytical equations of state, not reconstructed by the common-tangent construction, where the densities are then multiple-valued analytic functions of the activities, one would find that each of the curves in Figure 1 is associated with a second curve, not shown, which expresses z_2 as a function of ρ_2 in a dilute gas, again at the same fixed temperature T . These three curves also emerge from the origin $z_2 = \rho_2 = 0$ with a common slope, but this slope is now very close to 1, which, for solutes that are relatively insoluble in the liquid solvent, is very much less than the common slope $1/\Sigma$ of the liquid branches. The slope of these curves is now the limiting ratio of z_2 to ρ_2 in a dilute gas that is the nearly pure solvent vapor that is in equilibrium with the nearly pure liquid solvent. If it were not for a slight deviation from ideality in the vapor, that limiting ratio would be exactly 1.

Figure 2 shows, again schematically, the LVcoex curve of Figure 1, now together with its associated gas-phase branch,

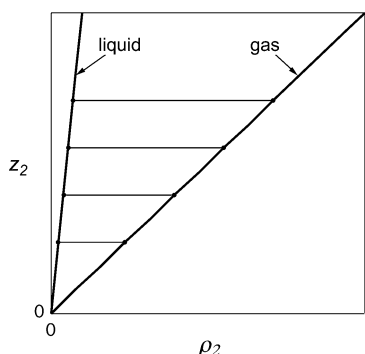


Figure 2. Schematic representation of the liquid and gas branches of the liquid–vapor coexistence curve in the ρ_2 , z_2 plane at fixed temperature, emphasizing only their initial slopes. That of the liquid branch is $1/\Sigma$ with a small Σ (large slope); that of the gas branch is close to 1. The horizontal lines are a few representative tielines connecting the coexisting phases indicated by dots.

and with horizontal tielines connecting coexisting phases. As remarked above, with the unreconstructed analytic equation of state, there will be such a vapor branch associated with each of the other two curves in Figure 1 as well, and the conjugate pair would look again, schematically, like the pair in Figure 2, but these would not be liquid–vapor coexistence curves. For example, a horizontal line connecting a point on the liquid branch of the fixed- z_1 curve to its conjugate point on the vapor branch would connect states of equal T , equal z_1 , and equal z_2 but unequal p , so these would not be coexisting phases; likewise, points on the fixed- p liquid and vapor curves connected by a horizontal line would be phases of equal T , equal z_2 , and equal p , but unequal z_1 , and thus would again not be coexisting phases. Instead, those gas phases would be metastable, not in stable equilibrium with the liquid. In stable phases, the pressure $p(z_1, z_2, T)$ is necessarily a single-valued function of z_1, z_2, T , but an unreconstructed analytical equation of state may, for example, yield a metastable phase with the same z_1, z_2, T as in a stable phase but at a different pressure. Even though we are interested here primarily in the properties of the liquid solution alone, this serves as a warning, for the analysis in section 3, that when the solvent activity $z_1(\rho_1, \rho_2, T)$ is inverted to yield ρ_1 as a function of z_1, ρ_2, T from an unreconstructed analytical equation of state, the resulting ρ_1 is multiple valued and one must identify its stable liquid branch.

Hill⁹ has addressed the question of the difference between the constant- z_1 and constant- p expansions. An alternative derivation is given here in the Appendix. The result is that, if we continue to denote by B the second osmotic virial coefficient in the expansion (8), and now by B' the analogous coefficient when the expansion is at fixed T and p instead of fixed T and z_1 , then

$$B = B' + \frac{1}{2}(v_2 - kT\chi) \quad (13)$$

where v_2 is the partial molecular volume of the solute at infinite dilution in the solvent and χ is the compressibility of the pure solvent ($z_2 = \rho_2 = 0$ in Figure 1). The volume v_2 is by definition the rate (positive or negative) at which the volume of the solution changes with increasing number of solute molecules at fixed p, T , and mass of solvent, and is thus identically also $\chi(\partial p/$

$\partial \rho_2)_{\rho_1, T}$ with χ the compressibility of the solution; so (13) may also be written

$$B = B' + \frac{1}{2}\chi \left[\left(\frac{\partial p}{\partial \rho_2} \right)_{\rho_1, T}^{\circ} - kT \right] \quad (14)$$

with χ now again the compressibility of the pure solvent.

Typical dense liquid solvents are so nearly incompressible that $kT\chi$ in (13) is almost always negligible compared with v_2 . With strongly solvophobic solutes, B may be very large and negative, much greater in magnitude even than the typically positive v_2 , so while B' may finally be slightly more negative than B it may perhaps not be by much. In the numerical illustration for propane in water in section 4, the coefficient B' is found to be only 6% more negative than B . Thus, $(\partial^2 z_2 / \partial \rho_2^2)_{T, p}^{\circ}$ may often be an acceptable approximation to $(\partial^2 z_2 / \partial \rho_2^2)_{T, z_1}^{\circ}$, but that is not true of the corresponding second derivative at liquid–vapor coexistence, where, as illustrated in Figure 1, it is likely even to be of the opposite sign.

3. B FROM $p(\rho_1, \rho_2, T)$

Most empirical equations of state for two-component fluid mixtures are unreconstructed analytic functions of the form $p = p(\rho_1, \rho_2, T)$ and include adjustable parameters usually evaluated by fitting to liquid–vapor equilibria. Here, we outline the method by which the $z_2(\rho_2, z_1, T)$ required for the evaluation of the second osmotic virial coefficient B via (8) may in principle be obtained from $p(\rho_1, \rho_2, T)$. Then, in section 4, this is carried out for the van der Waals two-component equation of state for illustration, with B then obtained numerically for propane in water at 25 °C as an example.

By a standard method, making use of the identity $(\partial F / \partial V)_{T, N_1, N_2} = -p$, where F is the Helmholtz free energy, V the volume, and N_1 and N_2 the numbers of molecules of the two species, one integrates $p(N_1/V, N_2/V, T) - (N_1/V + N_2/V)kT$ over V from a general V to $V = \infty$ with T, N_1 , and N_2 fixed. From the result of the integration, one has thereby obtained the difference between the Helmholtz free-energy density $f = F/V$ and the corresponding ideal-gas f_{ig} , as a function of the same variables ρ_1, ρ_2 , and T as in $p(\rho_1, \rho_2, T)$. With (3), one then has the identity

$$kT \ln \left(\frac{z_i}{\rho_i} \right) = \frac{\partial(f - f_{ig})}{\partial \rho_i} \quad (15)$$

and thus has $z_1(\rho_1, \rho_2, T)$ and $z_2(\rho_1, \rho_2, T)$.

The crucial step is now the inversion of $z_1 = z_1(\rho_1, \rho_2, T)$ to yield ρ_1 as a function of z_1, ρ_2, T :

$$\rho_1 = \rho_1(z_1, \rho_2, T) \quad (16)$$

This inverse function, as anticipated in section 2, is in general multiple valued, but from knowledge of the properties of the solvent, it is usually easy to discern which root is the density of the stable liquid, since there is usually a great difference between it and any other root. The inversion (16) must in practice be done numerically.

Having thus found $\rho_1(z_1, \rho_2, T)$, one then substitutes this into the previously obtained $z_2(\rho_1, \rho_2, T)$, so that z_2 is now expressed as a function of z_1, ρ_2, T :

$$z_2 = z_2[\rho_1(z_1, \rho_2, T), \rho_2, T] \quad (17)$$

We now have z_2 as the new function $z_2(\rho_2, z_1, T)$ of the required variables. Since $\rho_1(z_1, \rho_2, T)$ is generally known only numerically, so also now is $z_2(\rho_2, z_1, T)$, and the remaining calculation of B via the expansion in (8) or from (10) is then again done numerically. The numerical procedure is discussed in section 4 where it is illustrated with the two-component van der Waals equation.

Since the relation between B and B' in (13) and the equivalent (14) is exact and since χ , and v_2 or the equivalent $\chi(\partial p/\partial \rho_2)_{\rho_1, T}$ (section 2), are usually known from experiment or are readily calculable from $p(\rho_1, \rho_2, T)$, the required virial coefficient B can equally well be obtained from the constant- p expansion that yields B' :

$$z_2 = \frac{1}{\Sigma} \rho_2 (1 + 2B'\rho_2 + \dots) \quad (\text{fixed } p, T) \quad (18)$$

In that case, instead of inverting $z_1 = z_1(\rho_1, \rho_2, T)$ to obtain $\rho_1 = \rho_1(z_1, \rho_2, T)$, one would invert $p = p(\rho_1, \rho_2, T)$ to obtain $\rho_1 = \rho_1(p, \rho_2, T)$, which, when substituted into the known $z_2 = z_2(\rho_1, \rho_2, T)$, as before, now gives

$$z_2 = z_2[\rho_1(p, \rho_2, T), \rho_2, T] \quad (19)$$

This is z_2 as a function of ρ_2, p, T , which may be expanded in powers of ρ_2 at fixed p and T to yield B' via (18) and then B via (13) or (14).

A good strategy would be to calculate both B and B' from the respective expansions (8) and (18), and then to evaluate the (usually small) difference $B - B'$. When compared with the theoretical (13) or (14), with $v_2 = [\chi(\partial p/\partial \rho_2)_{\rho_1, T}]$ and χ known, it would provide an important check on the accuracy of the calculated B and B' .

4. ILLUSTRATION: B FROM THE VAN DER WAALS TWO-COMPONENT EQUATION OF STATE; PROPANE/WATER

The van der Waals equation of state for a one-component fluid of density ρ is

$$p = \frac{kT}{1/\rho - b} - a\rho^2 \quad (20)$$

It is then adapted as an equation of state for a two-component mixture with components of densities ρ_1 and ρ_2 by substituting

$$\rho = \rho_1 + \rho_2 \quad (21)$$

and taking a and b to be weighted averages of parameters a_{ij} and b_{ij} with weights that are quadratic in the densities:¹⁰

$$a = (\rho_1^2 a_{11} + 2\rho_1 \rho_2 a_{12} + \rho_2^2 a_{22})/(\rho_1 + \rho_2)^2 \quad (22)$$

$$b = (\rho_1^2 b_{11} + 2\rho_1 \rho_2 b_{12} + \rho_2^2 b_{22})/(\rho_1 + \rho_2)^2 \quad (23)$$

This is then a six-parameter equation of state, but it has the useful property that the parameters may be uniquely associated with the separate interactions: a_{11} and b_{11} from properties of the pure solvent, a_{12} and b_{12} from interactions of isolated solute molecules with the solvent, and a_{22} and b_{22} from the solute–solute interactions.

We introduce the dimensionless variables

$$\begin{aligned} \varpi &= \frac{b_{11}^2}{a_{11}} p, & t &= \frac{b_{11}}{a_{11}} kT, & D_1 &= b_{11} \rho_1, & D_2 &= b_{11} \rho_2, \\ \alpha &= a/a_{11}, & \beta &= b/b_{11} \end{aligned} \quad (24)$$

with a and b as in (22) and (23). The equation of state is then

$$\varpi = \frac{t}{1/(D_1 + D_2) - \beta} - \alpha(D_1 + D_2)^2 \quad (25)$$

We also define the dimensionless

$$\begin{aligned} A_{12} &= a_{12}/a_{11}, & A_{22} &= a_{22}/a_{11}, & B_{12} &= b_{12}/b_{11}, \\ B_{22} &= b_{22}/b_{11} \end{aligned} \quad (26)$$

so that

$$\alpha = (D_1^2 + 2D_1 D_2 A_{12} + D_2^2 A_{22})/(D_1 + D_2)^2 \quad (27)$$

$$\beta = (D_1^2 + 2D_1 D_2 B_{12} + D_2^2 B_{22})/(D_1 + D_2)^2 \quad (28)$$

The dimensionless activities

$$\zeta_1 = b_{11} z_1, \quad \zeta_2 = b_{11} z_2 \quad (29)$$

first as functions of the densities and temperature calculated from the equation of state (25) by the procedure outlined in section 3, are then

$$\begin{aligned} \zeta_1 &= \frac{D_1}{1 - \beta(D_1 + D_2)} \exp \left\{ \frac{1}{1/(D_1 + D_2) - \beta} \times \right. \\ &\quad \left. \left[1 + \frac{2B_{12} - B_{22} - 1}{(D_1/D_2 + 1)^2} \right] - \frac{2}{t} (D_1 + D_2 A_{12}) \right\} \\ \zeta_2 &= \frac{D_2}{1 - \beta(D_1 + D_2)} \exp \left\{ \frac{1}{1/(D_1 + D_2) - \beta} \times \right. \\ &\quad \left. \left[B_{22} + \frac{2B_{12} - B_{22} - 1}{(D_2/D_1 + 1)^2} \right] - \frac{2}{t} (D_1 A_{12} + D_2 A_{22}) \right\} \end{aligned} \quad (30)$$

The solubility Σ , which is the ratio $\rho_2/z_2 (=D_2/\zeta_2)$ in the limit of infinite dilution ($D_2 = 0$), follows from (31) with $\beta = 1$ from (28):

$$\Sigma = (1 - D_1) \exp \left[-\frac{1}{1/D_1 - 1} (2B_{12} - 1) + 2D_1 A_{12}/t \right] \quad (31)$$

A_{22} and B_{22} do not occur in Σ because it is a property only of the solvent and of the solvent's interaction with isolated solute molecules. The same is true of the partial molecular volume v_2 at infinite dilution. From the definition of v_2 in section 2 and from the equation of state in the form (25), the dimensionless $\rho_1 v_2$ at infinite dilution is

$$\begin{aligned} \rho_1 v_2 &= \frac{1 + 2D_1(B_{12} - 1) - 2D_1(1 - D_1)^2 A_{12}/t}{1 - 2D_1(1 - D_1)^2/t} \\ (D_2 &= 0) \end{aligned} \quad (32)$$

It may be verified that Σ in (32), the infinite dilution limit of v_2 in (33), and the compressibility χ of the pure solvent as calculated from (20), satisfy the thermodynamic identity¹¹

$$v_2/kT\chi \equiv 1 - (\partial \ln \Sigma / \partial \ln \rho_1)_T \quad (D_2 = 0) \quad (34)$$

where the derivative on the right-hand side measures by how much the solubility of the solute depends on the density of the solvent.

From ζ_2 as a function of the densities and temperature in (31), one could have added a fourth curve in Figure 1, viz., z_2 vs ρ_2 at fixed ρ_1 . That, too, would have started at the origin with the same slope $1/\Sigma$ as the others and with yet a different curvature, yielding a still different measure of the solvent-mediated effective interaction between solute molecules.

The calculation of the second osmotic virial coefficient B will follow from (30) and (31) by the procedure outlined in section 3. It is illustrated here for propane as solute in water at 25 °C.

The six parameters a_{ij} and b_{ij} must first be assigned. The a_{11} and b_{11} are fit from two experimentally known properties of the pure solvent, chosen here to be its density and vapor pressure at 25 °C. With superscripts L and G referring to the equilibrium liquid and gas phases, respectively, and with the liquid density ρ_1^L and equilibrium vapor pressure p_0 specified, the three equations $p^L = p^G = p_0$ and $z_1^L = z_1^G$ then determine ρ_1^G , a_{11} , and b_{11} . (The resulting $\rho_1^G = 7.6960 \times 10^{17}/\text{cm}^3$ is very close to $p_0/kT = 7.6940 \times 10^{17}/\text{cm}^3$; the slight difference is due to slight nonideality of the vapor.) We find

$$\begin{aligned} a_{11} &= 1.5038 \times 10^{-35} \text{ erg cm}^3, \\ b_{11} &= 2.7538 \times 10^{-23} \text{ cm}^3 \end{aligned} \quad (35)$$

(Had this been done at 0 °C instead of 25 °C, the resulting a_{11} and b_{11} would have been only slightly different: prefactors 1.56 and 2.78 instead of 1.50 and 2.75.)

The parameters a_{12} and b_{12} [or their dimensionless forms A_{12} and B_{12} from (26), since a_{11} and b_{11} are now known] are found by specifying two experimental properties of propane at infinite dilution in water at 25 °C. We take these to be the solubility Σ and the partial molecular volume v_2 , for which we adopt the values $\Sigma = 0.0372^{12}$ and $v_2 = 66.8 \text{ cm}^3/\text{mol}$.¹³ Then, with the known density of the liquid, we have from (32) and (33)

$$A_{12} = 1.6093, \quad B_{12} = 2.2887 \quad (36)$$

It remains to assign a_{22} and b_{22} (or the dimensionless A_{22} and B_{22} , since a_{11} and b_{11} are known). A frequently applied simplification of the van der Waals two-component equation of state is to take $b_{12} = (1/2)(b_{11} + b_{22})$ and $a_{12}^2 = a_{11}a_{22}$,¹⁰ but it is better to take these combining rules at a more molecular level and to recognize that b_{22} is a characteristic molecular volume, not diameter, and a_{22} is the product of a characteristic molecular interaction energy and volume, not an energy alone. Thus, with σ_{ij} the effective ij diameter and ε_{ij} the effective ij interaction energy parameter, we take

$$B_{22} = \left(\frac{\sigma_{22}}{\sigma_{11}}\right)^3, \quad A_{22} = \frac{\varepsilon_{22}}{\varepsilon_{11}} \left(\frac{\sigma_{22}}{\sigma_{11}}\right)^3, \quad A_{12} = \frac{\varepsilon_{12}}{\varepsilon_{11}} \left(\frac{\sigma_{12}}{\sigma_{11}}\right)^3 \quad (37)$$

and then approximate

$$\frac{\sigma_{12}}{\sigma_{11}} = \frac{1}{2} \left(1 + \frac{\sigma_{22}}{\sigma_{11}}\right), \quad \frac{\varepsilon_{22}}{\varepsilon_{11}} = \left(\frac{\varepsilon_{12}}{\varepsilon_{11}}\right)^2 \quad (38)$$

With A_{12} known in (36) and the ratio σ_{22}/σ_{11} of the "diameter" of a propane molecule to that of a water molecule to be specified, these will determine the required A_{22} and B_{22} . A literature consensus for the diameter σ_{22} of the propane molecule is 4.4 \AA ,^{14,15} and that for water, σ_{11} , is 2.75 \AA ,^{16–18} so $\sigma_{22}/\sigma_{11} = 1.60$. This then yields

$$A_{22} = 2.2015, \quad B_{22} = 4.096 \quad (39)$$

We could alternatively have specified $B_{12} = (\sigma_{12}/\sigma_{11})^3$ in addition to (37) and (38) instead of specifying the value of σ_{22}/σ_{11} . This would have implied $\sigma_{22}/\sigma_{11} = 2B_{12}^{1/3} - 1$, so with B_{12} known in (36) it would have implied $\sigma_{22}/\sigma_{11} = 1.635$ (close to the 1.63 from Ben-Amotz and Herschbach's estimates of σ_{22} and σ_{11} for propane and water¹⁸) instead of the 1.60 we adopted, and would also have altered A_{22} ; or, with $\sigma_{22}/\sigma_{11} = 1.60$ still, it would have implied $B_{12} = 2.197$ instead of the 2.2887 in (36). As this calculation of B is only illustrative, the choice among these alternatives could be more or less arbitrary. We proceed with A_{12} , B_{12} , A_{22} , and B_{22} in (36) and (39).

The next step is to evaluate ζ_1 from (30) at infinite dilution ($D_2 = 0$) with the prescribed t (corresponding to 25 °C in this illustration) and with D_1 of the pure solvent under its vapor pressure. That will then be the ζ_1 that is fixed. One then prescribes a very small value of D_2 in the liquid phase and solves (30) with the prescribed t , ζ_1 , and D_2 to obtain the corresponding value of D_1 in the liquid. Two criteria for the choice of D_2 must be met. It must be small enough so that $2|B|\rho_2 [=2(|B|/b_{11})D_2]$ with the ultimately calculated osmotic coefficient B is very much less than 1. Otherwise, the numerically evaluated second derivative $(\partial^2 z_2/\partial \rho_2^2)_{t,\zeta_1}$ in (10), from which B is found, will not be close enough to its value at infinite dilution; i.e., the higher order terms in the expansion (8) will affect the estimate of B . But D_2 must also be large enough so that $(z_2/\rho_2)\Sigma$ is distinguishable from its value 1 at infinite dilution, i.e., so that the fixed- z_1 curve in Figure 1 has a discernible curvature, distinguishable from the straight line $z_2 = \rho_2/\Sigma$. For the present illustration, we find that values of D_2 in the range $1 \times 10^{-6} \leq D_2 \leq 3 \times 10^{-4}$ easily meet these criteria. Any D_2 in that range ultimately yields the same B , and with that B and with D_2 at the high end of that range, $-2B\rho_2$ is found to be only 0.02.

The required root D_1 in the liquid phase that is calculated as above for the chosen value of D_2 and the fixed ζ_1 and t is easily distinguished as the largest root and is always very close to its value in the pure liquid solvent under its vapor pressure. But that very small difference between the D_1 calculated for the given D_2 and its limiting ($D_2 = 0$) value is important and must be kept careful track of. This D_1 and the corresponding D_2 are then substituted into ζ_2 in (31). The result is the value of ζ_2 ($=b_{11}z_2$) for any such chosen D_2 ($=b_{11}\rho_2$) at the fixed ζ_1 ($=b_{11}z_1$) and t ($=b_{11}kT/a_{11}$).

When D_2 is small, the resulting ζ_2 differs very little from D_2/Σ with the known Σ , but it is that difference that determines B , which is obtained as $B/b_{11} = (1/2)(\zeta_2\Sigma/D_2 - 1)/D_2$. As long as D_2 has been chosen from an appropriate range as described above, and as long as the corresponding ζ_2 is calculated with high precision with the precisely calculated D_1 , the resulting value of B will be independent of the chosen D_2 .

Here, with the values of the parameters as chosen above, this procedure yields

$$B/b_{11} = -34, \quad B = -570 \text{ cm}^3/\text{mol} \quad (40)$$

It may be compared with the $B = -668 \text{ cm}^3/\text{mol}$ calculated for propane in water at 25 °C by Liu and Ruckenstein¹⁹ by a different method and with the much more elaborate UNIQUAC²⁰ and Wang-Chao²¹ equations of state.

As explained in section 3, to obtain the corresponding coefficient B' in the expansion of z_2 at fixed p and T , one first inverts p instead of z_1 to obtain ρ_1 in terms of ρ_2 , p , and T but otherwise follows the same procedure as above. In this way, we

calculate $B'/b_{11} = -36$, so that $B/b_{11} - B'/b_{11} = 2$. As anticipated, the difference is small. With the b_{11} in (35), the $v_2 = 66.8 \text{ cm}^3/\text{mol}$ ($=1.109 \times 10^{-22} \text{ cm}^3/\text{molecule}$) we assumed earlier, and with $kT\chi$ negligible compared with v_2 , we thus find these B and B' to satisfy the identity (13) exactly, to the present numerical precision.

In this example, the solubility Σ was already known because its experimental value was used as one of the data in setting the parameters a_{12} and b_{12} . That may not always be so, and when it is not, one prescribes the values of D_2 in pairs, fits the resulting ζ_2 to a quadratic of the form $cD_2 + dD_2^2$, and then identifies $\Sigma = 1/c$ and $B/b_{11} = d/(2c)$. When that is done here, the c that is found merely reproduces the already known $1/\Sigma$.

The van der Waals equation of state with the b_{22} we have been assuming may also be used to estimate the gas-phase second virial coefficient of pure propane vapor at 25°C , with the result $B_{\text{gas}} = -416 \text{ cm}^3/\text{mol}$, to be compared with the experimental $-393 \text{ cm}^3/\text{mol}$.²² Comparing these with the osmotic B , we see that the effect of the mediation of the solvent is to increase the effective strength of the solute–solute attraction, as measured by $-B$, by somewhat more than $1/3$ of its value in vacuum. There has long been interest in such comparisons.^{23–27}

Since the parameters in this equation of state were partly chosen to fit experimentally measured properties, it might be anticipated that it could now give a reasonable account of other properties for which it was not specifically designed. We test this here by calculating the liquid branch of the liquid–vapor coexistence curve in the x_2 (mole fraction of propane)–pressure plane at low x_2 , with temperature fixed, to compare with the measurements of Chapoy et al.²⁸ Coexistence is now determined by solving simultaneously the four equations $p^G = p^L = p_0$, $z_1^G = z_1^L$, $z_2^G = z_2^L$ for $\rho_1^G, \rho_2^G, \rho_1^L, \rho_2^L$ with p_0 specified, or, alternatively, for $\rho_1^G, \rho_2^G, \rho_1^L, p_0$ with x_2^L specified. Again, one chooses for ρ_1^L the root ρ_1 that is close to that of pure water, and then the required x_2^L is $\rho_2^L/(\rho_1^L + \rho_2^L)$. We do this for $T = 298.15 \text{ K}$, and in Figure 3, we plot the calculated x_2^L (called x_2 in the plot) vs p_0 (called p in the plot), along with the data of Chapoy et al. (nominally at $T = 298.12 \text{ K}$, but that should not make a visible difference). The extrapolation of both the calculated and experimental data to $x_2 = 0$ was done subject to the two conditions that the calculated and experimental curves must enter $x_2 = 0$ at the same p because the vapor pressure of pure water was one of the data used in setting the values of a_{11} and b_{11} , and that they must do so with the same limiting slope because that slope is determined by the solubility Σ , the experimental value of which was one of the data used in setting the values of a_{12} and b_{12} . The two curves agree well.

5. SUMMARY AND DISCUSSION

We have outlined the scheme by which, from an equation of state of the form $p = p(\rho_1, \rho_2, T)$ for a solution of a solute at density ρ_2 in a solvent of density ρ_1 at temperature T , one may derive the solute activity z_2 in the form $z_2 = z_2(\rho_2, z_1, T)$. That then allows z_2 to be expanded in powers of ρ_2 at fixed solvent activity z_1 and temperature. From the McMillan–Mayer solution theory, that is what is needed if one is to identify the second osmotic virial coefficient from the coefficient of the second-order term in the expansion. It gives a first correction to the ideal-dilute solution laws (Henry's law and the van 't Hoff osmotic-pressure law), which hold in the limit of infinite dilution. It is noted that the coefficient of the second-order term in an expansion of z_2 in powers of ρ_2 with T fixed but with

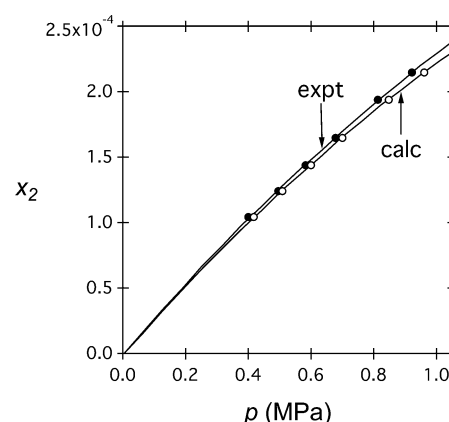


Figure 3. The liquid branch of the liquid–vapor coexistence curve in the x_2 (mole fraction of propane) p plane at 25°C . The points on the curve marked expt are the experimental data of Chapoy et al.²⁸ for propane in water; those on the curve marked calc are as calculated here with the van der Waals two-component equation of state with the same parameters as in the calculation of the second osmotic virial coefficient. The two curves have the same initial slope, and both extrapolate at $x_2 = 0$ to the vapor pressure of pure water at this temperature. This limiting pressure is indistinguishable from 0 on the scale of the plot. At the pressures at which the data are plotted, the equilibrium vapor is mostly propane.

a second constraint other than that of fixed z_1 is also a measure, but a different one, of the effective solute–solute interactions responsible for the deviations from the ideal-dilute solution laws. In Figure 1 are sketched z_2 as a function of ρ_2 at fixed T for each of three different additional constraints: that of fixed z_1 , that of liquid–vapor equilibrium, and that of fixed pressure. The three share a common initial slope, $1/\Sigma$, where we refer to Σ as the solubility of the solute in the liquid solvent. But of these three, it is only that of fixed z_1 for which the second derivative $\partial^2 z_2 / \partial \rho_2^2$ evaluated at $\rho_2 = 0$ yields the second osmotic virial coefficient, directly related to the integral of the solute–solute pair correlation function at infinite dilution.

Earlier calculations of B in the literature, including those referenced here, are undoubtedly correct or are reasonable approximations. What has been done here is first to outline the logic of the calculation, in general terms in section 2 and then for the analytical equations of state in section 3, before the detailed numerical calculations are done in section 4. This we believe makes clear the path by which the ultimately calculated osmotic coefficient follows from its definition.

With B the osmotic virial coefficient and with B' the analogous coefficient when the expansion of z_2 is at fixed p instead of at fixed z_1 , one finds, following an earlier analysis by Hill,⁹ the identity $B \equiv B' + (1/2)(v_2 - kT\chi)$, where v_2 is the partial molecular volume of the solute at infinite dilution and χ is the compressibility of the pure solvent. For low-solubility solutes, where B and B' may be large and negative, $v_2 - kT\chi$ is usually much smaller in magnitude than either B or B' , so B' may sometimes be an acceptable approximation to B .

The scheme for obtaining $z_2(z_1, \rho_2, T)$ from an equation of state in the form $p = p(\rho_1, \rho_2, T)$ and then identifying B is illustrated with the two-component van der Waals equation and applied to propane in water at 25°C . We chose this equation of state for illustrating the general method because it is the one most transparently related to molecular properties with the fewest adjustable parameters. It may be thought of as the mean-field approximation to the equation of state of a mixture of

attracting hard spheres with the simplest approximation for the hard-sphere part. Once its parameters are chosen to reproduce some key experimental quantities, the remaining thermodynamic properties calculated with it are likely to be realistic even with liquids as complex as water. For serious applications, one would choose more refined equations of state, but for illustrating general principles, which was our aim, this has proved adequate.

This equation of state has six parameters: a_{11} and b_{11} from properties of the pure solvent, a_{12} and b_{12} from the interaction of isolated solute molecules with the solvent, and a_{22} and b_{22} from the solute–solute interactions. Here the first pair is identified from the experimental density and vapor pressure of water; the second pair from the experimental solubility Σ and partial molecular volume v_2 of the solute; and the third pair from relations of the form $b_{22}/b_{11} = (\sigma_{22}/\sigma_{11})^3$ and $a_{ij} = (\epsilon_{ij}/\epsilon_{11})(\sigma_{ij}/\sigma_{11})^3$, the usual combining rules for the σ_{ij} and ϵ_{ij} and the known diameters of the water and propane molecules.

In this way, we calculated $B/b_{11} = -34$ ($B = -570 \text{ cm}^3/\text{mol}$) and $B'/b_{11} = -36$ for propane in water at 25°C , so B' more negative than B by only 6%. With the same parameters, we found the gas-phase second virial coefficient of pure propane to be $-416 \text{ cm}^3/\text{mol}$ (as compared with the experimental $-393 \text{ cm}^3/\text{mol}$), so the effect of the mediation of the solvent is to increase the effective strength of the solute–solute attraction, as measured by $-B$, by more than $1/3$ over that in vacuum. Again with the same parameters and at the same temperature, we calculated the mole fraction x_2 of the solute in the liquid solution in equilibrium with its vapor as a function of the equilibrium pressure p and compared it in Figure 3 with the experimental measurements of Chapoy et al.²⁸ They agree closely enough to give additional credence to the second osmotic virial coefficient we calculated when illustrating with the van der Waals equation of state how to extract that coefficient from $p = p(\rho_1, \rho_2, T)$.

APPENDIX

We here derive eq 13 for the difference $B - B'$ between the second osmotic virial coefficient B obtained from the expansion of z_2 in powers of ρ_2 at fixed z_1 and T , and the analogous coefficient B' obtained when z_2 is expanded instead in powers of ρ_2 at fixed p and T .

Here we use the chemical potential μ_1 instead of z_1 . Start with the partial derivative identity

$$(\partial\psi/\partial\rho_2)_{T,\mu_1} \equiv (\partial\psi/\partial\rho_2)_{T,p} - (\partial\psi/\partial p)_{T,\rho_2}(\partial\mu_1/\partial\rho_2)_{T,p} / (\partial\mu_1/\partial p)_{T,\rho_2} \quad (\text{A.1})$$

which holds for any intensive $\psi(\rho_2, p, T)$, and apply this identity twice, first when it is z_2 that is taken to be the function ψ and then when it is $(\partial z_2/\partial\rho_2)_{T,\mu_1}$. The result is the partial derivative identity

$$\begin{aligned} (\partial^2 z_2/\partial\rho_2^2)_{T,\mu_1} &= Z_{22} - 2Z_{2p}m_2/m_p - Z_p m_{22}/m_p \\ &\quad + 2Z_p m_2 m_{2p}/m_p^2 \\ &\quad - (-Z_{pp}m_2/m_p + Z_p m_2 m_{pp}/m_p^2)m_2/m_p \end{aligned} \quad (\text{A.2})$$

where Z is z_2 and m is μ_1 , both taken to be functions of ρ_2 , p , and T , and where subscripts 2 and p then mean differentiation of these functions with respect to ρ_2 and to p , respectively.

Now go to the limit of infinite dilution, $\rho_2 = 0$. In this limit, Z_p and Z_{pp} are both 0. There are several ways to see this, probably the simplest from the expansion $z_2 = (\rho_2/\Sigma)(1 + 2B'\rho_2 + \dots)$ in (18), which is with p and T fixed. Both Σ and B' vary as functions of those p and T but are independent of ρ_2 . Then Z_p , which is $(\partial z_2/\partial p)_{T,\rho_2}$, and Z_{pp} , which is $(\partial^2 z_2/\partial p^2)_{T,\rho_2}$, are both of order ρ_2 and therefore vanish as $\rho_2 \rightarrow 0$. The quantities that are multiplied by Z_p and Z_{pp} in (A.2) all remain finite in the $\rho_2 = 0$ limit, so in that limit, (A.2) becomes

$$\left(\frac{\partial^2 z_2}{\partial\rho_2^2}\right)_{T,\mu_1}^\circ = Z_{22}^\circ - 2Z_{2p}^\circ \frac{m_2^\circ}{m_p^\circ} \quad (\text{A.3})$$

where the superscript $^\circ$ again means the limit $\rho_2 = 0$. The left-hand side of (A.3), from (8), is $4B/\Sigma$, while Z_{22}° from (18), is $4B'/\Sigma$, so

$$B = B' - \frac{1}{2}\Sigma Z_{2p}^\circ m_2^\circ/m_p^\circ \quad (\text{A.4})$$

But $m_2^\circ \equiv (\partial\mu_1/\partial\rho_2)_{T,p}^\circ = -kT/\rho_1$ (Raoult's law), while $m_p^\circ \equiv (\partial\mu_1/\partial p)_{T,\rho_2}^\circ$. The latter derivative in the $\rho_2 = 0$ limit is just $(\partial\mu_1/\partial p)_T$ in the pure solvent, which is $1/\rho_1$. Thus, (A.4) becomes

$$B = B' + \frac{1}{2}kT\Sigma Z_{2p}^\circ \quad (\text{A.5})$$

It remains to evaluate $Z_{2p}^\circ \equiv (\partial^2 z_2/\partial\rho_2\partial p)_{T,\rho_2=0}^\circ$. From (18), it is $-(1/\Sigma^2)(\partial\Sigma/\partial p)_{T,\rho_2}$, which by thermodynamic identity¹¹ is $(v_2 - kT\chi)/(kT\Sigma)$, where v_2 is the partial molecular volume of the solute at infinite dilution and χ is the compressibility of the pure solvent. Thus,

$$B = B' + \frac{1}{2}(v_2 - kT\chi) \quad (\text{A.6})$$

This is (13), as required.

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Notes

The authors declare no competing financial interest.

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