Concentration Dependence of Linear Self-Assembly and Exactly Solvable Models

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Exactly solvable one-dimensional models of amphiphilic solutions are used to investigate the concentration dependence of isodesmic chemical equilibria (linear self-assembly). Highly efficient methods are developed for solving directly for the equation of state and for obtaining the cluster statistics. Remarkably, at fixed pressure, it is the *low* concentration limit where the equilibrium constant is both maximized and shows the strongest concentration dependence. [S0031-9007(96)01125-8]

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A famous paradigm in statistical mechanics is that there can be no phase transition in a one-dimensional short-ranged model [1]. This implies that one should not rely on standard mean field concepts when trying to interpret quasi-one-dimensional phenomena, such as linear self-assembly. Consider, as an example of a chain forming amphiphilic solution, a two-component (AB) mixture where the solute(A)-solvent(B) interaction is purely repulsive and has the same range as the attractive AA and BB interactions. As the temperature (T) is lowered, longer and longer chains of solute are formed, but since the cost of breaking a given chain is, at most, restricted to two unfavorable AB interactions, the entropy of mixing is sufficient to prevent any phase transition to an infinite cluster. In fact, such a model is an exact representation of isodesmic chemical equilibria [2]; i.e., an exponential distribution of clusters defined by a single equilibrium constant (K). This language hides the fact that, at fixed temperature and, say, pressure (p), there still remains one thermodynamic degree of freedom in a two-component mixture. Thus, even if K were constant for a particular pair of fixed thermodynamic fields, it could not then be independent of concentration (x) in any other phase space. Just what does our intuition expect for the concentration dependence of an equilibrium constant? In the pure case, density dependence can only arise from cluster-cluster interactions, which typically lead to an increase in K as density rises. One might be tempted to naively apply this scenario to solution equilibria and surmise that K will be a true constant at sufficiently low solute concentration (i.e., in the absence of cluster-cluster interaction). However, a recent simulation study of a model discotic amphiphile in solution found precisely the opposite behavior [3]. Attard has interpreted at least part of the simulation picture by noting that at fixed pressure the overall density must decrease as solute is added, or, in the language of colloidal science, the solvent pressure must decrease [4]. This implies that the low concentration limit will be at least a local maximum in the equilibrium constant. If the effect even partly approached the significance observed in simulation, this result would hold important implications for experiments on chain forming surfactants and possibly even polymerization in solution. In fact, there already exists as yet unexplained data on a particular discotic amphiphile, demanding a significant concentration dependence to isodesmic chemical equilibria at low x [5]. This Letter addresses the above general issue in physical chemistry by asking what is predicted by exactly solvable one-dimensional models. Although methods for solving for the partition function of such models have long been available [1], here I shall develop a highly efficient approach for extracting the exact equation of state and the equilibrium cluster distribution, with an absolute minimum of mathematical effort. At no stage do I require algebra beyond the solutions of a quadratic equation, and the results needed to describe isodesmic chemical equilibria can be given particularly simple analytic forms.

Any model in liquid state physics is formally solved by potential distribution theory. In either the canonical ensemble [6] or, as required here, the grand canonical ensemble [7], one knows that the chemical potential of species A is given by the sum rule

$$\rho_A(\mathbf{r})e^{-\mu_A+v_A^{\text{ext}}(\mathbf{r})} = \langle e^{-\psi_A(\mathbf{r})}\rangle . \tag{1}$$

Hereafter, units are chosen such that all lengths are given in terms of a hard-core diameter (and deBroglie wavelengths set to unity) and all energies and free energies in units of k_BT (with k_B Boltzmann's constant). The symbols ρ, μ, and v^{ext} denote number density, chemical potential, and external field, respectively. The right side of Eq. (1) is the average of a Boltzmann factor involving the energy of a test particle of type A placed at the position $\mathbf{r}$; i.e., ψ is the energy of interaction between the test particle and the fluid, but the test particle does not actually interact with the system. For all models involving a hard-core contribution to the test-particle interaction, one can split this average into two factors:

$$P_c(\mathbf{r})\langle e^{-\psi_A(\mathbf{r})}\rangle_c , \tag{2}$$

where the first factor is the probability of inserting the hard core of a real particle into the fluid at position $\mathbf{r}$, and the Boltzmann factor average is now to be carried out in the presence of a hard core fixed at **r**; hence the subscript c, which, in one-dimensional systems, I shall write as w (for wall). The hard-core factor controls phenomena such as the freezing of hard sphere systems, whereas Ising symmetry transitions are entirely concerned with the second factor; an average of attractive energies in the presence of a hard cavity. In any dimension, the first factor is trivially written down for lattice-gas (LG) models; in the pure fluid case it is just $(1-\rho)$. In one dimension the Boltzmann factor average is also exactly solvable, because the presence of a hard-core (wall) splits the system into two independent ensembles (given finite-range interactions unable to reach across the wall). Accordingly, consider a symmetric two-component LG in one dimension, with equal AA and BB attractive well depths (denoted ϵ) and the AB interaction purely repulsive; in particular, let us work explicitly with the case in which the AB repulsive range is two lattice units. From potential distribution theory, one can write down the exact solution of this model (and similar models) almost by inspection:

$$x e^{-\mu_A} = f[1-(1-x_w)\rho_w + a x_w \rho_w]^2, \tag{3}$$

$$(1-x)e^{-\mu_B} = f[1-x_w\rho_w + a(1-x_w)\rho_w]^2, \tag{4}$$

$$x_w\rho_w e^{-\mu_A} = (1-\rho_w)[1-(1-x_w)\rho_w + a x_w\rho_w], \tag{5}$$

$$(1-x_w)\rho_w e^{-\mu_B} = (1-\rho_w)[1-x_w\rho_w + a(1-x_w)\rho_w], \tag{6}$$

where the subscript w denotes a quantity belonging to a lattice site adjacent to a hard wall, and for convenience I have introduced $a = e^{\epsilon} - 1$ and $f = (1-\rho)/\rho$; $\rho = \rho_A + \rho_B$, $x = \rho_A/\rho$, etc. To obtain these results I have applied potential distribution theory to measure the chemical potentials in three classes of systems: (I) the homogeneous fluid mixture, (II) adjacent to a hard wall inserted into the mixture, and (III) adjacent to repulsive walls that act as an ordinary hard wall to one component but repel the other component one additional lattice site further away (these are the hard cores of our particular model mixture). To see how this works consider the derivation of Eq. (3). First, in system (I) the hard core factor on the right side of Eq. (2) is $(1-\rho)[1-(1-x_w)\rho_w]^2$, where the squared factor arises from the fact that type B must be excluded from the lattice site either side of type A. The Boltzmann factor average is by inspection $(1 + a\rho_{wAB})^2$ determined by the density of type A next to the inner hard wall of the cavity inserted to make system (III). Now, consider the measurement in system (II), where the hard core factor is $(1-\rho_w)[1-(1-x_w)\rho_w]$ and the Boltzmann factor average is $(1 + a\rho_{wAB})$; there are no longer any squared factors because the hard wall excludes interactions with everything to, say, the left. Finally, the same analysis applied to the measurement in system (III) yields

$$\rho_{wAB} e^{-\mu_A} = (1-\rho_{wAB})[1-(1-x_w)\rho_w] \times (1 + a\rho_{wAB}), \tag{7}$$

and so comparison with the analogous equation from system (II), at identical μ_A, yields a result for ρ_{wAB} in terms of x_w and ρ_w. Equation (3) then follows immediately from substitution into the result of the measurement in system (I) and Eq. (5) from the same substitution applied to the measurement in system (II). Equations (4) and (6) arise from evaluating the chemical potential of B particles (solvent), in precisely the same way, and, of course, are trivially related to Eqs. (3) and (5) by the symmetry of the model.

An efficient method of solving Eqs. (3)–(6) follows by dividing (3) by (5) and (4) by (6), giving

$$x_w\rho_w f[1-(1-x_w)\rho_w + a x_w\rho_w] + x\rho_w = x, \tag{8}$$

$$(1-x_w)\rho_w f[1-x_w\rho_w + a(1-x_w)\rho_w] + (1-x)\rho_w = 1-x, \tag{9}$$

which add to give

$$\rho_w f\{1 - 2x_w(1-x_w)\rho_w + a\rho_w[x_w^2 + (1-x_w)^2]\} + \rho_w = 1. \tag{10}$$

For example, if we want solutions within the phase space (T, ρ, x), simply choose the desired values of a and f and then for any x_w one has ρ_w from Eq. (10) as the solution of a simple quadratic, which can then be substituted in, say, Eq. (8) to trivially solve for x (as x_w is varied from 0 to 1, so does x). Alternatively, if one wants to work at fixed solvent chemical potential, (T, μ_B, x) phase space, then choose a and μ_B and obtain ρ_w as a function of x_w from the quadratic equation defined by (6), then insert into (10) to get f (i.e., ρ) and then finally into (8) to get x. The phase space (T, p, x), beloved of physical chemists, is even more trivial to analyze, because one can prove the exact sum rule [8]

$$p = -\ln(1-\rho_w), \tag{11}$$

which immediately gives, for any x_w, the density from (10) and then x from (8). The fact that one never needs to solve anything beyond a quadratic equation is consistent with the absence of phase transitions in one dimension; in fact, there is never more than one physical root defined by demanding ρ_w to lie between 0 and 1. In the limits of x_w tending to zero or unity, the above analysis reduces to the well known exact solution for the one-dimensional Ising model [1], usually solved by transfer matrix methods to get the partition function which can then be differentiated to obtain the order parameter (ρ), yielding the inverse of the equation of state obtained directly from potential distribution theory. The simple model mixture in which the AB repulsion is identical to AA and BB repulsive interactions is also readily solved; one gets Eq. (10), from class (I) and (II) measurements alone, except that the middle term in brackets on the left side is absent, together with (3)–(6), (8), and (9) minus the corresponding terms.

Let us now turn to the cluster analysis needed to obtain the concentration dependence of the isodesmic chemical equilibria $[1] + [n - 1] = [n]$, where $[n]$ denotes the concentration of chains of solute (type A) exactly n particles long; I shall denote the corresponding aggregate density as ρ_n. The density of isolated solute is defined by the conditional probability that, given a solute present at one site, then there is no other solute directly on either side of it; i.e.,

$$\rho_1 = x\rho(1 - \rho_{wAB}^{A})^2, \tag{12}$$

where the superscript on yet another wall density indicates that the wall arises from a frozen solute. To obtain ρ_n, note from, say, periodic boundary conditions that $x\rho$ is the probability of placing the left end of any cluster, and then building a chain of length n simply introduces $n - 1$ factors of the probability ρ_{wAB}^{A}, which hereafter is denoted by the symbol Y. Thus, one arrives at an exact model of isodesmic chemical equilibria ($K_n = K, n = 2, 3, ...$):

$$\rho_n = \rho_1 Y^{n-1}, \qquad K = Y/\rho_1 . \tag{13}$$

The single quantity Y defines the entire cluster distribution, $\rho_n = \rho_A(1 - Y)^2 Y^{n-1}$, and note that this gives yet another demonstration of why there can be no phase transition; i.e., for any $Y < 1$ the significance of the largest clusters are always exponentially damped. The quantity $-\ln K$ defines the configurational free energy change when a monomer joins a chain, while the configurational free energy per monomer of an infinite chain (no ends) is $\mu_\infty^0 = \mu_A - \ln Y$. This physical chemistry language is reviewed, for example, in Ref. [3]; here, let us use our exactly solvable model to explore the concentration dependence of these quantities. To obtain the key quantity Y in terms of our solution for the equation of state, one needs to evaluate the chemical potential μ_A at the inner wall defined by freezing a solute particle:

$$Ye^{-(\mu_A + \epsilon)} = (1 - Y)[1 - (1 - x_w)\rho_w](1 + a\rho_{wAB}) . \tag{14}$$

This is precisely the same use of potential distribution theory used to derive the equation of state, with the minor difference that the wall now presents an attractive field (of magnitude ϵ). Comparison with the evaluation of μ_A at an ordinary hard wall leads immediately to a linear equation defining Y in terms of a, x_w, and ρ_w:

$$Y = \frac{(1 + a)x_w\rho_w}{[1 - (1 - x_w)\rho_w + ax_w\rho_w]} . \tag{15}$$

Inserting this expression into the definition of μ_∞^0 and Eqs. (12) and (13) for the equilibrium constant, and simplifying using Eqs. (5) and (8), respectively, one arrives at the following physically appealing results:

$$\mu_\infty^0 = -\epsilon + p , \tag{16}$$

$$\ln K = \epsilon + p - \ln(1 - \rho) . \tag{17}$$

The significance of constant pressure to the isodesmic chemical equilibria defined by our LG model is now clearly exposed. Whereas fixing T and p leads to constant μ_∞^0, this then demands a significant concentration dependence to $\ln K$, arising from the final term in Eq. (17). The first two terms on the right side contribute to the enthalpy change on adding one monomer to a given chain, while the entropy change is therefore contained within the $\ln(1 - \rho)$ term. It is straightforward to use the above equations to obtain the x dependence of the enthalpic and entropic contributions to $\ln K$. The concentration dependence of the density at fixed temperature and fixed pressure (equivalent to fixed ρ_w) follows directly from Eq. (10), and is significant whenever the solute-solvent repulsive interactions play a key role; note that when maintaining a fixed pressure the volume of the whole system decreases when a monomer moves into a chain. For liquid state values of T and p, the density and hence $\ln K$ drops very rapidly as solute is added at low concentration, partly because of the nonlinear relation between x and x_w in this region. Thus, not only is the equilibrium constant a maximum at lowest concentration, but, in addition, so is its variation with x. The symmetry of our model is manifest in Eq. (10), forcing ρ to be symmetric about $x = x_w = 1/2$, where it is a minimum. From (17) it follows that, at constant pressure, $\ln K$ displays these same properties [9]. The drop in $\ln K$ as x is varied from 0 to $1/2$ is easily obtained from Eqs. (10) and (17):

$$\Delta \ln K = \ln\left(\frac{2}{1 + \frac{1-\rho_w^2}{1+a\rho_w^2}}\right) . \tag{18}$$

For any fixed T (p) this expression is monotonic in p (T). The maximum possible change is $\ln 2$, with a typical value being at least half of this. A typical liquid state value for the drop in density is about 0.1 [10].

In conclusion, exactly solvable one-dimensional models have an interesting story to tell concerning the concentration dependence of isodesmic chemical equilibria. One finds that at fixed pressure it is the low concentration limit where K shows the strongest dependence on x and reaches at least a local maximum. This explicitly vindicates the phenomenological analogy with colloidal science, introduced by Attard [4], although the effect is significantly stronger than the linear behavior that Attard obtains from an effective medium approximation to general one-dimensional models. Clearly, the above scenario is a key part of the story observed in simulation [3], although the magnitude of the total drop (but not the initial rate of drop) is much less spectacular. In particular, the symmetry inherent in the above model is not applicable to the moderate-to-high concentration region of the simulations, where the three-dimensional nature appeared to take over. Namely, in the simulation study, $\ln K$ continued to fall and ρ_1 never peaked, even at high concentration, where isotropic solutions resembled a jumble of short chains, presumably because the three-dimensional freedom allowed for significant shielding of chain ends (note that these states were readily generated by melting lyotropic columnar liquid crystal phases, as well as by aggregation of dispersed monomers). Thus, whether or not the low concentration behavior of one-dimensional models represents the full story behind simulation and experiment awaits an extension of the above methods to obtain the self-assembly of one-dimensional aggregates *within* higher-dimensional systems. The efficient methods described above for extracting this type of information may well have general applicability to a range of important conceptual issues in physical chemistry.

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[1] See, for example, C.J. Thompson, *Mathematical Statistical Mechanics* (Princeton University, Princeton, NJ, 1972).

[2] D. Fennell-Evans and H. Wennerström, *The Colloidal Domain* (VCH, New York, 1994), p. 136.

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[6] B. Widom, J. Chem. Phys. **39**, 2808 (1963).

[7] J.R. Henderson, Mol. Phys. **50**, 741 (1983).

[8] The pressure is defined by the Gibbs-Duhem equation, which we can write as $-(1 + f)\partial p/\partial \rho_w = e^{\mu_A}\partial(xe^{-\mu_A})/\partial \rho_w + e^{\mu_B}\partial[(1 - x)e^{-\mu_B}]/\partial \rho_w$, and then use Eqs. (3) and (4) to rewrite entirely in terms of a, f, x_w, and ρ_w. If one then evaluates the quantity $(1 + f)\partial \ln(1 - \rho_w)/\partial \rho_w$, via repeated use of Eq. (10), one proves equivalence, i.e., sum rule (11). This LG sum rule is the direct equivalent of the continuum result $p = \rho_w$.

[9] In the simple two-component mixture model, where AB repulsion is identical to the AA and BB repulsive interaction, the result (17) is modified [in contrast to Eq. (16)], and, in particular, the symmetry of K about $x = 1/2$ is lost. However, the same qualitative trend in $\ln K$ is seen at low concentration, it is just that the magnitude of the drop is less and the minimum value of K shifts to $x < 1/2$. All of the analysis does, of course, apply in the pure fluid (Ising model) limit $x_w = 1$.

[10] At moderate fixed pressure $[\rho_w^2 < \sqrt{2}/(1 + \sqrt{2})]$ the maximum drop in density occurs at finite T [at $1 + a = \sqrt{2}\,(\rho_w^{-2} - 1)$] and is $1/[(1 + \sqrt{2})^2(1 + \rho_w)]$.