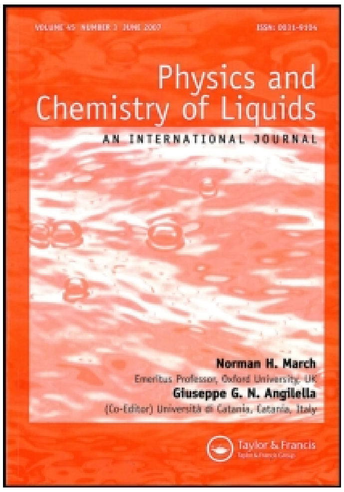

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Chemical Equilibrium Laws in a Lattice Model of Dilute Associated Solutions†

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Chemical equilibrium laws are discussed within the framework of the grand canonical ensemble and for lattice models of dilute solutions of aliphatic alcohols in a nonpolar solvent. A statistical interpretation of association constants in a lattice model and their connection with lattice model parameters are given and discussed.

1 INTRODUCTION

It is well known that properties of associated solutions can be successfully interpreted in terms of chemical equilibria between the complexes in solution.[1,2] In the course of our investigations on the dilute solutions of aliphatic alcohols[3] we have discovered a surprising lack of values of association constants even for systems so widely investigated. In fact, almost all published values of equilibrium constants were obtained by fitting an assumed model of association to thermodynamic data. Therefore a theoretical evaluation and discussion of these quantities is needed and in this and following papers we examine what information can be extracted from the lattice models.

Having considered a lattice model for solutions of aliphatic alcohols in nonpolar solvents,[4] we discuss now the chemical equilibria between complexes. In particular, we show how the "chemical reactions" can be defined without introducing additional assumptions and how the equilibrium constants and the appropriate activities can be introduced in the statistical description of these systems without affecting the true value of partition function of the

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system. As a final result we obtain a statistical interpretation of association constants in a lattice model and their connection with lattice model parameters which can be directly calculated. Some examples are given.

2 GENERAL ASSUMPTIONS AND ASSOCIATION CONSTANTS IN A LATTICE MODEL

Consider a dilute solution of associating substance A (aliphatic alcohol) in a nonpolar solvent S. The A and S molecules are distributed on a lattice of coordination number z, so that all lattice sites are occupied. The lattice is rigid and does not exert any pressure ($p = 0, pV = 0$). In the lattice model the continuous range of possible orientations of molecules is replaced by a number of discrete orientations and all molecules are supposed to have contact points ready to interact with contact points of nearest neighbours.[5] The total intermolecular potential energy is a sum of interactions of nearest neighbour lattice sites. Recently a possibility of nearest neighbour edge–edge interaction was also considered[6] in a different context.

Each molecule A is a r-mer occupying r lattice sites and having I, O and H contact points, each molecule S is a monomer with z I contact points, occupying one lattice site. The associating substance A forms complexes A_i from i monomers A_1. The chemical reactions can be written

$$\begin{aligned} A_1 + A_{i-1} &\rightleftarrows A_i \qquad K_i(i = 2, 3, 4, \ldots) \\ A_1 + A_{i-1} &\rightleftarrows A_{ic} \qquad K_{ic}(i = 3, 4, \ldots) \end{aligned} \tag{1}$$

where index c refers to cyclic complexes.

A thermodynamic treatment in the theory of chemical association is based on the assumption that all associated complexes are in mutual equilibrium.[1] This leads to the equality of the respective chemical potentials.

$$\begin{aligned} \mu_i &= \mu_{i-1} + \mu_1 \\ \mu_{ic} &= \mu_{i-1} + \mu_1 \end{aligned} \tag{2}$$

If

$$\mu_k = \mu_k^\ominus + RT \ln a_k^* \qquad k = 1, 2, 3, 3c, \ldots$$

the equilibrium constants

$$K_i^\ominus = \frac{a_i^*}{a_{i-1}^* a_1^*} \qquad K_{ic}^\ominus = \frac{a_{ic}^*}{a_{i-1}^* a_1^*} \tag{3}$$

can be related to $\mu_k^\ominus$'s in a standard way.[1] Here a_k^* is the activity of complex A_k, $\mu_k^\ominus$ = the standard chemical potential of A_k referred to the infinite dilution, R = the gas constant, T = absolute temperature, i = number of molecules A_1 in one molecule A_k.

In the lattice models of solutions a concentration of the given chemical species A_k is usually represented by its dimensionless density[4] ρk

$$\rho_k \equiv \frac{N_k}{B}$$

where N_k is the number of molecules of component A_k, and B = the number of lattice sites.

The respective ratios of these densities are defined as the apparent association constants (K_j) of reactions (1)

$$K_i = \frac{\rho_i}{\rho_{i-1}\rho_1} \quad . \quad K_{ic} = \frac{\rho_{ic}}{\rho_{i-1}\rho_1} \tag{4}$$

As we dilute a solution, expressions (4) tend to the respective limiting values K_j^∞

$$\lim_{\rho_A \to 0} K_j = K_j^\infty = K_j^\ominus \tag{5}$$

K_j^∞ are the true association constants, equal to the thermodynamic equilibrium constants $K_j^\ominus$.

3 STATISTICAL DERIVATION OF CHEMICAL EQUILIBRIUM CONSTANTS

The physical cluster expansion for the thermodynamic properties of a reactive fluid, with a detailed attention for systems composed of monomers and dimers, was developed by Lawson and Dahler[7] who extended the earlier works of Hill *et al.*[8] Ebeling[9] generalised the Lawson's and Dahler's fugacity expansion, deriving in a statistical way the mass-action law for interacting gases and plasmas.

In this section we discuss the chemical equilibrium laws for the lattice model of a solution of an aliphatic alcohol A in a nonpolar solvent S within the framework of the grand canonical ensemble. Our system is composed of succesive associated complexes A_k, in quantities N_k, and of N_S nonassociated molecules S, occupying together $B = N_S + \sum_k r_k N_k$ lattice sites. Under the constraint of a constant B the modified grand canonical partition function Ξ^* is

$$\Xi^* \equiv \frac{\Xi}{\lambda_S Z_S} = \sum_{\{N_k\}} Z(\{N_k\}, B, T) \prod_k a_k^{N_k} \tag{6}$$

where Ξ is the nonmodified grand canonical partition function, Z_S = the canonical partition function of the pure S lattice, $Z(\{N_k\}, B, T)$ = the canonical partition function of the solution, divided by Z_S, as implied by Eq. (6). Also

$$a_k \equiv \frac{\lambda_k}{\lambda_S^{r_k}}$$

where λ_k and λ_S are the absolute activities of complex A_k and solvent S, respectively; connected with the chemical potentials μ_k and μ_S in the usual manner

$$\lambda_k = \exp(\beta\mu_k),\ \lambda_S = \exp(\beta\mu_S),\ \beta = 1/(kT)$$

r_k being the number of lattice sites occupied by the given complex A_k.

Formula (6) may be rewritten by grouping together terms according to the number of N_k's different from zero, thus

$$\Xi^* = 1 + \sum_{l=1} Z_l a_l + \sum_{l=1} \sum_{m=1} Z_{lm} a_l a_m + \cdots$$

where the indexes l, m refer to the chemical species present in the system and

$$Z_l \equiv Z(N_l = 1) \tag{7}$$

$$Z_{lm} \equiv \begin{cases} Z(N_l = 2) & l = m \\ Z(N_l = 1, N_m = 1) & l \neq m \end{cases}$$

etc.

and all other N_k are equal to zero.

The expansion of $\ln \Xi^*$ is then obtained as follows

$$\begin{aligned}\frac{1}{B}\ln \Xi^* = {} & d_1 a_1 + d_2 a_2 + d_3 a_3 + d_{3c} a_{3c} + d_4 a_4 + \cdots \\ & + d_{11} a_1^2 + d_{12} a_1 a_2 + d_{13} a_1 a_3 + \cdots \\ & + d_{111} a_1^3 + \cdots \\ & + \cdots .\end{aligned} \tag{8}$$

where

$$d_k = \frac{Z_k}{B}$$

$$d_{1k} = \begin{cases} \dfrac{(Z_{1k} - Z_1 Z_k)}{B} & k \neq 1 \\[2ex] \dfrac{(Z_{11} - (\tfrac{1}{2})Z_1^2)}{B} & k = 1 \end{cases} \tag{9}$$

$$d_{111} = \frac{(Z_{111} - Z_1 Z_{11} + (\tfrac{1}{3})Z_1^3)}{B}$$

Densities of the individual complexes A_k can be obtained from the known relations[8]

$$\rho_k \equiv \frac{\bar{N}_k}{B} = \frac{1}{B}\left(\frac{\partial \ln \Xi^*}{\partial \ln a_k}\right)_{B,T,a_{j\neq k}} \tag{10}$$

It follows immediately from Eqs. (8) and (10) that

$$\rho_k = d_k a_k + \sum_{l=1}(\cdots)a_k a_l + \cdots \tag{11}$$

and in the limit of the infinite dilution

$$\rho_k = d_k a_k \qquad (\rho_k \to 0)$$

We introduce now the relative activities a_k^* (or the individual associated complexes A_k)

$$a_k^* \equiv a_k d_k \tag{12}$$

so that at infinite dilute solution they become equal to the respective densities ($a_k^* \to \rho_k$ when $\rho_A \to 0$). Now we can use the particular form of the conditions of chemical equilibrium as given by Eqs. (2); hence

$$a_k = (a_1)^i \qquad k = 2, 3, 3c, \ldots$$

Here i denotes the number of molecules A_1 in the complex A_k, and

$$\frac{a_k^*}{a_1^{*i}} = \frac{d_k}{d_1^i} = K_{(k)}^{\ominus} = K_{(k)}^{\infty} \tag{13}$$

Thus we have derived relations connecting association constants with quantities d_k. The expressions for chemical equilibrium constants were obtained recently by Ebeling[9] who used a theory of clusters in a one component system. Our quantity d_k corresponds to Ebeling's cluster coefficient $b_{|k|}$ related to bound states of k molecules. His derivation is based on a division of each partition function into subsums corresponding to bound and to free states, and on the principle that bound states must be treated as composite molecules. Having treated *ab initio* our system as a multicomponent one we did not need to perform such divisions. On the contrary we can group certain terms together so as to recover the virial expansion for a one solute system. But, in any case an unequivocal definition as to which state in a system is called a dimer, which—a trimer and so on, is neccessary. Such definition is not always possible;[10] however, in the case of a lattice model we can use as a criterion the intermolecular energy equal to

$$n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \cdots$$

Here n_i are positive integers and ε_i = real numbers corresponding to assumed interaction energies between molecules and their contact points.

4 STATISTICAL INTERPRETATION OF ASSOCIATION EQUILIBRIUM CONSTANTS

A comparison of Eqs. (3) and (13) allows one to express the equilibrium constants of reactions (1) in terms of the respective quantities d_k

$$K_i^{\ominus} = K_i^{\infty} = \frac{d_i}{d_{i-1}\, d_1} \qquad i = 2, 3, \ldots$$

$$K_{ic}^{\ominus} = K_{ic}^{\infty} = \frac{d_{ic}}{d_{i-1}\, d_1} \qquad i = 3, 4, \ldots$$

Then, using the relation (9), we connect association constants with the canonical partition functions Z_k

$$\begin{aligned} K_i^{\ominus} &= K_i^{\infty} = \frac{Z_i}{Z_{i-1} Z_1} B \\ K_{ic}^{\ominus} &= K_{ic}^{\infty} = \frac{Z_{ic}}{Z_{i-1} Z_1} B \end{aligned} \tag{14}$$

This is only as it should be, because the constants refer to infinite dilution. The canonical partition function is represented by

$$Z_k = j_k(T) j_S(T)^{-r_k} Q_k; \qquad Q_k = G_k(B) \exp(-\beta E_k)$$

where $j_k(T)$ and $j_S(T)$ are the internal partition functions of complex A_k and molecule S, respectively, Q_k = the configurational partition function approximated by a lattice with one molecule A_k and $(B - r_k)$ molecules S, E_k = the intermolecular potential energy referred to the pure S lattice and $G_k(B)$ = the number of configurations which one molecule A_k may take up on a lattice of B sites.

Therefore, under the following assumptions:

1) $j_k(T) = j_1(T)^i \exp(-\beta n \varepsilon_{OH}),\ n = \begin{cases} i-1 & \text{for open complexes} \\ i & \text{for cyclic complexes} \end{cases}$

where i denotes a number of molecule A_1 in one molecule A_k and ε_{OH} = the energy of hydrogen bond.

2) I contact points of the solvent and of the hydrocarbon part of alcohol molecule are identical.

Eqs. (14) become

$$K_i^{\ominus} = K_i^{\infty} = \frac{g_i}{g_{i-1} g_1} \eta \tag{15}$$

$$K_{ic}^{\ominus} = K_{ic}^{\infty} = \frac{g_{ic}}{g_{i-1}g_1}\eta^2 \tag{16}$$

where $\eta = \exp[-\beta(w_{\mathrm{OH}} - w_{\mathrm{OI}} - w_{\mathrm{HI}})]$, $w_{\mathrm{OH}} \equiv \varepsilon_{\mathrm{OH}} - \varepsilon_{\mathrm{II}}$ is related to association interaction of alcohol, $w_{\mathrm{OI}} \equiv \varepsilon_{\mathrm{OI}} - \varepsilon_{\mathrm{II}}$ and $w_{\mathrm{HI}} \equiv \varepsilon_{\mathrm{HI}} - \varepsilon_{\mathrm{II}}$ are related to interaction of alcohol with solvent, ε_{ij} is the energy of interaction between "i" and "j" contact points, $g_k = G_k/B$ = number of configurations of molecule A_k per one lattice site.

Equations (15) and (16) show combinatorial factors appearing as an entropic contribution and the energy factor, determined here by the hydrogen bond energy and interaction energies between alcohol and solvent molecules. Formula (16) contains one η factor more than formula (15) because a cyclic r-mer has one hydrogen bond more than an open r-mer. Thus we obtain a possibility of calculating association constants if we can calculate the combinatorial factors g_k.

5 VIRIAL COEFFICIENTS OF THE SOLUTE—SOLVENT SYSTEM

Now we seek the connection of the multicomponent description with McMillan-Mayer virial expansion for a solute A in a solvent S.

Consider the well known activity expansion of the modified grand canonical partition function Ξ^*

$$\frac{1}{B}\ln \Xi^* = \frac{1}{B}\ln\left[1 + \sum_{N_A \geq 1} Q_{N_A} a^{N_A}\right] = \sum_{l \geq 1} b_l a^l \tag{17}$$

The coefficients b_l are the lattice cluster sums expressed in terms of configurational partition functions Q_{N_A}

$$Bb_1 = Q_1$$
$$Bb_2 = Q_2 - (\tfrac{1}{2})Q_1^2$$
$$Bb_3 = Q_3 - Q_1Q_2 + (\tfrac{1}{3})Q_1^3$$
etc.

and the configurational partition function is defined by

$$Q_{N_A} = \sum_E G(E, N_A, B)\exp[-\beta(E - E_S)]$$

where $G(E, N_A, B)$ denotes the number of configurations of a system composed of N_A molecules A and $(B - r_A N_A)$ molecules S at the given energy E and for the given number of lattice sites B, and E_S = the energy of the pure S lattice. It follows from Eqs. (10) and (16) that

$$\rho \equiv \frac{\bar{N}_A}{B} = \frac{1}{B}\left(\frac{\partial \ln \Xi^*}{\partial \ln a}\right)_{B,T} = \sum_{l \geq 1} l b_l a^l$$

The corresponding density series for the thermodynamic potential, is

$$\frac{1}{B}\ln \Xi^* = \rho - \beta_2\rho^2 - 2\beta_3\rho^3 - \cdots$$

where

$$\beta_2 = \frac{b_2}{b_1^2}, \qquad \beta_3 = \frac{b_3}{b_1^3} - \frac{2b_2^2}{b_1^4}, \qquad \text{etc.} \tag{18}$$

We can obtain the form of Eq. (17) from the "multicomponent" grand canonical partition function by using the equalities (8), (12) and grouping together terms with the same powers of a_1^*. The activity a in Eq. (17) is the activity of monomers, a_1^*, divided by the cluster coefficient b_1. In this way we find

$$\begin{aligned} b_2 &= b_1^2\left(\frac{d_2}{d_1^2} + \frac{d_{11}}{d_1^2}\right) \\ b_3 &= b_1^3\left(\frac{d_{3c}}{d_1^3} + \frac{d_3}{d_1^3} + \frac{d_{12}}{d_1^3} + \frac{d_{111}}{d_1^3}\right) \end{aligned} \tag{19}$$

where quantities d's have been defined by Eqs. (9). Specializing, we have

$$d_1 = \frac{(Z(N_1 = 1))}{B}$$

$$d_2 = \frac{(Z(N_2 = 1))}{B}$$

$$d_3 = \frac{(Z(N_3 = 1))}{B}$$

$$d_{3c} = \frac{(Z(N_{3c} = 1))}{B}$$

$$d_{11} = \frac{(Z(N_1 = 2) - (\frac{1}{2})Z(N_1 = 1)^2)}{B}$$

$$d_{12} = \frac{(Z(N_1 = 1, N_2 = 1) - Z(N_1 = 1)Z(N_2 = 1))}{B}$$

$$d_{111} = \frac{(Z(N_1 = 3) - Z(N_1 = 1)Z(N_1 = 2) + (\frac{1}{3})Z(N_1 = 1)^3)}{B}$$

Using the definitions (13), Eqs. (19) may be rewritten as

$$\begin{aligned} b_2 &= b_1^2\left(K_2^\infty + \frac{d_{11}}{d_1^2}\right) \\ b_3 &= b_1^3\left[K_2^\infty(K_{3c}^\infty + K_3^\infty) + \frac{d_{12}}{d_1^3} + \frac{d_{111}}{d_1^3}\right] \end{aligned} \tag{20}$$

The substitution of Eqs. (20) in Eqs. (18) gives the connection of the virial coefficients of the density series with association constants

$$\beta_2 = K_2^\infty + \frac{d_{11}}{d_1^2}$$

$$\beta_3 = K_2^\infty(K_{3c}^\infty + K_3^\infty) - 2K_2^{\infty 2} - 4K_2^\infty \frac{d_{11}}{d_1^2} + \frac{d_{12}}{d_1^3} + \frac{d_{111}}{d_1^3} - \left(\frac{d_{11}}{d_1^2}\right)^2$$

As an explicit example let us consider a particularly simple case of one-energy association (i.e., $\varepsilon_{OO} = \varepsilon_{HH} = \varepsilon_{II} \neq \varepsilon_{OH}$) and two interaction energies (ε_{HI}, ε_{OI}) between the solvent and the chain molecules of alcohol. We have made some explicit calculations for Q_i, b_i, and β_i for $i \leq 3$. Several subsets of configurations appear in a natural way in the b_j's and their numbers are denoted by g_α, $g_{\alpha\beta}$, $g_{\alpha\beta\gamma}$. First, g_1 is the number of configurations (per one lattice site) of one monomer (one alcohol molecule), g_2 is for a dimer formed of two alcohol moecules connected by a hydrogen bond, g_3 is for a linear trimer (three alcohol molecules with three hydrogen bonds) and g_{3c} is for a cyclic trimer (three molecules with three hydrogen bonds). Then g_{11} is the number of configurations of two monomers overlapping not completely (by not all segments), g'_{111} is of three monomer molecules overlapping simultaneously but not completely (so that the Mayer f_{ij} is functions that are equal to -1, -1, -1), g''_{111} is of three monomer molecules overlapping not simultaneously and none of three pairs completely. Finally g_{12} is a sum of all nonphysical configurations of three molecules, any two of which are in a configuration of a dimer.

After tedious but straightforward calculations, d's can be expressed in terms of the g's. Thus

$$\frac{d_{11}}{d_1^2} = -\frac{g_2}{g_1^2} + \frac{(-g_1 - g_{11})}{g_1^2}$$

$$\frac{d_{12}}{d_1^3} = -\frac{\eta(g_{12} + 3g_{3c} + 2g_3)}{g_1^3}$$

$$\frac{d_{111}}{d_1^3} = \frac{((\frac{4}{3})g_1 + 4g_{11} + 2g'_{111} + g''_{111} + g_{12} + 2g_{3c} + g_3)}{g_1^4}$$

Here $\eta = \exp[-\beta(\varepsilon_{OH} + \varepsilon_{II} - \varepsilon_{OI} - \varepsilon_{HI})]$.

Now we can express β_2 and β_3 in terms of the g's. Grouping together terms corresponding to the association constants, defined in Eqs. (15), (16) and terms corresponding to athermal β_2^{ath} and β_3^{ath}, we finely obtain

$$\beta_2 = K_2^{\infty} - \kappa_2 + \beta_2^{\text{ath}} \tag{21}$$

$$\beta_3 = K_2^{\infty}[K_{3c}^{\infty} + K_3^{\infty} - 2K_2^{\infty} - 3\kappa_{3c} - 2\kappa_3 + 4\kappa_2 - 4\beta_2^{\text{ath}}]$$

$$+ \kappa_2[2\kappa_{3c} + \kappa_3 - 2\kappa_2 + 4\beta_2^{\text{ath}}] - \frac{(\eta - 1)g_{12}}{g_1^3} + \beta_3^{\text{ath}}$$

where

$$\beta_2^{\text{ath}} = \frac{(-g_1 - g_{11})}{g_1^2}$$

and

$$\beta_3^{\text{ath}} \simeq \frac{(g_1(2g'_{111} + g''_{111}) - (\frac{2}{3})g_1^2 - 2g_{11}^2)}{g_1^4}$$

are the athermal virial coefficients, to which the virial coefficients reduce by putting all interaction energies ε_{ij} equal to zero. Also κ_2, κ_3, κ_{3c} are the limiting values of association constants in an athermal solution,

$$\kappa_2 = (K_2^{\infty})_{\text{ath}} = (K_2^{\infty})_{\eta=1} = \frac{g_2}{g_1^2}$$

$$\kappa_3 = (K_3^{\infty})_{\text{ath}} = (K_3^{\infty})_{\eta=1} = \frac{g_3}{(g_2 g_1)}$$

$$\kappa_{3c} = (K_{3c}^{\infty})_{\text{ath}} = (K_{3c}^{\infty})_{\eta=1} = \frac{g_{3c}}{(g_2 g_1)}$$

The dimerization constant corresponds to a nonathermal part of the second virial coefficient, which includes configurations of two bound alcohol molecules and no configuration of two non-bonded ones. Equation (21) can be rewritten as

$$\beta_2 - \beta_2^{\text{ath}} = K_2^{\infty} - (K_2^{\infty})_{\text{ath}}.$$

The trimerization constants (K_3^{∞}, K_{3c}^{∞}) appear in a nonathermal contribution to the third virial coefficient, which has no simple interpretation and includes also overlapping configurations of two and three molecules, as is seen from the derivation of β_3 above.

6 ASSOCIATION CONSTANTS OF ALCOHOLS IN TWO DIMENSION LATTICE MODEL OF ALCOHOL SOLUTION

Basing on formulas (15) and (16) an illustrative calculation was carried out for a certain two-dimensional model. This model assumes the square lattice ($z = 4$) and the Barker model of alcohol molecule.[5] Each molecule of non-polar solvent S occupies one lattice site and has z contact points, called I (inert) contact points. Each alcohol molecule has one terminal segment with $(z - 1)$ I contact points, $(r - 2)$ segment with $(z - 2)$ I contact points and one terminal OH segment which is supposed to have two O contact points and one H contact point. The H contact point is taken as the point in direction perpendicular to the C—O bond. This model does not predict cyclic trimers. The calculated values of K_2^∞ and K_3^∞ for several succesive n-alcohols from homology series are summarized in Table I.

In an infinite dilute solution densities ρ_k go into mole fractions x_k and association constants expressed in mole fractions and in densities are equal ($K_p^\infty = K_x^\infty$). So all values presented in Table I may be treated as K_x^∞. The association constants of alcohols, K_2^∞ and K_3^∞, decrease with the increase of the number of carbon atoms in n-alcohol molecule. This fact can be understood qualitatively. The longer is the molecule of alcohol, the greater are the steric hinderances for the i-th alcohol molecule, which is to form a hydrogen bond with $(i - 1)$ molecules and as a final effect the relative number of configuration, $g_i/(g_{i-1}g_1)$, decreases with the length of chain of n-alcohol molecule. If the molecules of secessive alcohols are represented on a lattice by rigid, non-flexible r-mers, the association constants K_2^∞ and K_3^∞ do not depend on the value of r (i.e., the number of carbon atoms in n-alcohol molecule). The dimerization and trimerization constants (for the same alcohol) differ very slightly (at most 15%) and practically may be considered as equal. We can also see the influence of solvent on association constants. The association constants decrease with an increase of interaction between solvent and associating substance molecules, represented by energies $\varepsilon_{\mathrm{OI}}$ and $\varepsilon_{\mathrm{HI}}$.

7 DISCUSSION

Considering a lattice model for the dilute solutions of aliphatic alcohols in a nonpolar solvent we have derived in a statistical way the relations connecting association constants with the lattice cluster sums d_k. Recently the similar expressions were obtained for gases and plasmas by Ebeling.[9] Ebeling reated a system composed of the successive complexes as a one component

TABLE I

Association constants of *n*-alcohols in a two-dimension Barker model (in the units of dimensionless density $\rho = N/B$).

$\eta = 2788$ corresponds to $t = 25°\text{C}$, $\varepsilon_{OH} = -19665$ J/mol[11], $\varepsilon_{OI} = \varepsilon_{HI} = \varepsilon_{II} = 0$
$\eta = 848.2$ corresponds to $t = 25°\text{C}$, $\varepsilon_{OH} = -19665$ J/mol, $\varepsilon_{OI} = \varepsilon_{HI} = 0.1\varepsilon_{OH} = -1966$ J/mol, $\varepsilon_{II} = 0.05\varepsilon_{OH} = -983$ J/mol
$\eta = 258.1$ corresponds to $t = 25°\text{C}$, $\varepsilon_{OH} = -19665$ J/mol, $\varepsilon_{OI} = \varepsilon_{HI} = 0.2\varepsilon_{OH} = -3933$ J/mol, $\varepsilon_{II} = 0.1\varepsilon_{OH} = -1966$ J/mol

		K_2^∞			K_3^∞		
r	Lattice analog of	$\eta = 2788$	$\eta = 848.2$	$\eta = 258.1$	$\eta = 2788$	$\eta = 848.2$	$\eta = 258.1$
2	methanol	1502	457.0	139.1	1690	514.2	156.5
3	ethanol	1294	393.6	119.8	1171	356.3	108.4
4	*n*-propanol	1071	325.7	99.12	927.9	282.13	85.90
5	*n*-butanol	1036	315.2	95.90			
6	*n*-pentanol	948.8	288.7	87.84			
7	*n*-hexanol	920.5	280.0	85.21			
8	*n*-heptanol	864.1	262.9	79.79			
9	*n*-octanol	843.6	256.7	78.10			
10	*n*-nonanol	805.1	244.9	74.53			

system and used a division of the canonical partition functions Z_N into the subsums corresponding to bound and to free states of N molecules.

We considered the alcohol solution in a nonpolar solvent as a multicomponent system and we, conversely, group together terms with the same power of the activity of monomers. In this way we pass from the expansion of the logarithm of the multicomponent grand partition function to the virial expansion for a one solute–solvent system. We found the connections between the cluster sums and the virial coefficients (of density and of the activity series) also introducing the association constants K_j^{∞}.

The introduction of the association constants into a statistical description of the system, without affecting the true values of partition functions, does not require any additional assumptions. The only concern is an unambiguous definition as to which configuration in a system is classified as a dimer, which—as a trimer and so on. Such definition is not always possible in general,[10] but for the lattice model no difficulties with the division of the phase space are encountered. The association constants in a lattice model were expressed in terms of the lattice model parameters: combinatorial factors g_k appearing as an entropic contribution and the energy factor determined by the association energy and the interaction energies between alcohol and solvent molecules. This straightforward statistical interpretation of association constants has a practical significance because we can calculate them provided that the combinatorial factors g_k are known.

As can be seen from Eqs. of §5, the reducible cluster sums b_k occurring in the activity expansion as well as the irreducible cluster sums β_k occurring in the density expansion can be related to the association constants K_j^{∞}, the limiting values of the association constants in an athermal system and cluster sums in a nonathermal system. First, no significant simplification is seen when comparing b_k/b_1^k with β_k. Secondly, the simplicity of the division of $b_2/b_1^2 = \beta_2$ is lost already for β_3 (involving three molecules). The full expression for β_3 contains also an unwanted term with g_{12}. Therefore one can not hope for a simple representation of β_k into association contribution.

Let us remark that a formal introduction of multimerization into the activity series, i.e., assigning all gas imperfections to chemical reactions, will lead in general to negative concentrations of some species A_k. The same, mutatis mutandis, applies to the osmotic pressure McMillan–Mayer virial expansion.

The introduction of the lattice model allowed us to push calculations for enough to obtain a variety of results for the association constants, which were discussed in details in §6. Although the lattice model is not a good approximation to the liquid state in any sense, it did reveal already some interesting trends and regularities. In a forthcoming paper we expect to extend our calculations to several different representations of the assumed mode of association. In particular, we hope to discuss the cyclic associates and compare the simple lattice models with a multisite model which attempts at keeping the stereochemistry of CH_3OH relatively undistorted.

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