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Self-Associating Systems. III. Multinomial Theory for Ideal Systems Using the *z*-Average Molecular Weight*

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ABSTRACT: A general expression for the calculation of equilibrium constants of self-associating systems of ideal systems using the *z*-average molecular weight has been established. The derivations make use of the multinomial theorem but represent an independent method from that described (Derechin, M. (1968), *Biochemistry 7*, 3253) for use with the number, M_n, and weight-average, M_w, molecular weights.

In a previous paper (Derechin, 1968) self-association reactions of the type

$$nP_1 \rightleftarrows a_2P_2 + a_3P_3 + \cdots + a_mP_m$$

with

$$\sum_{i=2}^{m} ia_i = n \qquad (1)$$

for ideal systems have been examined. In that work, equations for the calculation of equilibrium constants from experimentally determined values of the number- and weight-average molecular weights were derived making use of multinomial theory. In this paper an independent theory that uses the same formal approach as before was derived for the analysis of self-association reactions using the *z*-average molecular weight.

Theoretical

It is assumed here that all species participating in the self-associating reaction have the same partial specific volume ($\bar{v}_1 = \bar{v}_2 = \cdots = \bar{v}$) and the same refractive index increment $(dn/dc_1)_{T,P} = (dn/dc_2)_{T,P} = \cdots = (dn/dc)_{T,P}$ and that the activity coefficient of each associating species can be represented by a series expansion as

$$\ln y_i = iBM_1c + \text{higher power of } c \qquad (2)$$

where B is the virial coefficient, M_1 is the molecular weight of the monomer, and c is the total solute concentration. At low solute concentration the higher powers in c are neglected. In the particular case, $i = 1$

$$\ln y_1 = BM_1c \qquad (2a)$$

Using eq 2 and 2a and the nomenclature of Adams and Fujita (1963), the concentration of each associating species and the total solute concentration, respectively, for a system at equilibrium can be stated as

$$c_i = K_i\frac{y_1^{\,i}}{y_i}c_1^{\,i} = K_ic_1^{\,i} \qquad i = 1, 2, \ldots \qquad (3a)$$

and

$$c = \sum_{i=1}^{m} K_ic_1^{\,i} \qquad i = 1, 2, \ldots \qquad (3)$$

By virtue of eq 3, $K_1 = 1$. Differentiating eq 3 and rearranging we have

$$\frac{dc}{dc_1} = \sum_{i-1}^{m} iK_ic_1^{\,i-1} \qquad (4)$$

The *z*-average molecular weight, M_{zc}, is defined here following suggested nomenclature of Adams and Williams, (1964); the subscript c is added to M_z to indicate a concentration dependent quantity. Thus

$$M_{zc} = \frac{\Sigma c_iM_i^{\,2}}{\Sigma c_iM_i} = \frac{M_1\Sigma i^2c_i}{\Sigma ic_i} \qquad (5)$$

Using eq 3a, 4, and 5, we can write

$$\frac{M_{zc}dc}{M_1} = \sum_{i=1}^{m} i^2K_ic_1^{\,i-1}dc_1 \qquad (6)$$

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which after integration becomes

$$I(c) = \int_0^c \frac{M_{zc}\mathrm{d}c}{M_1} = \sum_{i=1}^{m} K_i \int_0^{c_1(c)} i^2 c_1^{\,i-1}\mathrm{d}c_1 = \sum_{i=1}^{m} iK_i c_1^{\,i} \quad (7)$$

Expanding $I(c)$ in powers of c (Maclaurin's theorem) and using eq 3 we have

$$I(c) = \sum_{r=0}^{\infty} \frac{1}{r!}\left(\frac{\mathrm{d}^{(r)}I}{\mathrm{d}c^r}\right)_{c=0}\left[\sum_{i=1}^{m} K_i c_1^{\,i}\right]^r = \sum_{i=1}^{m} iK_i c_1^{\,i} \quad (8)$$

The power term in brackets in eq 8 can be evaluated by making use of multinomial theorem (see Parzen, 1960) as shown before (Derechin, 1968). Then eq 8 becomes

$$\sum_{\xi=1}^{m}\sum_{r=1}^{\xi} \frac{1}{r!}\left(\frac{\mathrm{d}^{(r)}I}{\mathrm{d}c^r}\right)_{c=0} G(\xi, r, K_i)c_1^{\,\xi} = \sum_{\xi=1}^{m} \xi K_\xi c_1^{\,\xi} \quad (9)$$

where

$$G(\xi, r, K_i) = \sum_{\alpha_2=0}^{r}\cdots\sum_{\alpha_m=0}^{r} \binom{r}{\left(\xi - \sum_{i=2}^{m} i\alpha_i\right), \alpha_2, \ldots \alpha_m} \prod_{i=2}^{m} K_i^{\alpha_i}$$

$$\xi = \sum_{i=1}^{m} i\alpha_i = \alpha_1 + \sum_{i=2}^{m} i\alpha_i$$

$\alpha_1, \alpha_2, \ldots, \alpha_m$ take all positive integral values for which

$$\xi - r = \sum_{i=2}^{m} (i-1)\alpha_i \qquad \text{condition 1}$$

$$\xi - \sum_{i=2}^{m} i\alpha_i \geq 0 \qquad \text{condition 2}$$

and

$$\sum_{i=1}^{m} \alpha_i = r \qquad \text{condition 3}$$

Comparing the coefficients of the same power of c on both sides of eq 9, we have

$$\sum_{r=1}^{\xi} \frac{1}{r!}\left(\frac{\mathrm{d}^{(r)}I}{\mathrm{d}c^r}\right)_{c=0} G(\xi, r, K_i) = \xi K_\xi \quad (10a)$$

or

$$\sum_{r=1}^{\xi} \frac{1}{r!}\left(\frac{\mathrm{d}^{(r)}I}{\mathrm{d}c^r}\right)_{c=0} \times\left[\sum_{\alpha_2=0}^{r}\cdots\sum_{\alpha_m=0}^{r}\binom{r}{\left(\xi - \sum_{i=2}^{m} i\alpha_i\right), \alpha_2, \ldots, \alpha_m} \times \prod_{i=2}^{m} K_i^{\alpha_i}\right] = \xi K_\xi \quad (10)$$

with conditions 1, 2, and 3 applicable, as in eq 9. Equation 10 represents a set of equations from which the equilibrium constants, $K_1, K_2, \ldots, K_m$, can be determined using the z-average molecular weight.

Application of the Theory to Calculation of Equilibrium Constants. Examining eq 10 we can see that $r!$ is simultaneously multiplying all summation terms (since it is in the multinomial coefficient) and dividing these terms as well ($1/r!$ precedes the derivative). Thus, the number $r!$ can be deleted from eq 10. Also, noting that

$$\left(\frac{\mathrm{d}^{(r)}I}{\mathrm{d}c^r}\right)_{c=0} = \left(\frac{\mathrm{d}^{(r-1)}I}{\mathrm{d}c^{r-1}}\right)_{c=0} = \left(\frac{\mathrm{d}^{(r-1)}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c^{r-1}}\right)_{c=0} \quad (11)$$

one can substitute the third form of eq 11 for the first in eq 10. Thus, eq 10 becomes

$$\sum_{r=1}^{\xi}\left(\frac{\mathrm{d}^{(r-1)}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c^{r-1}}\right)_{c=0} \times\left[\sum_{\alpha_2=0}^{r}\cdots\sum_{\alpha_m=0}^{r}\binom{1}{\left(\xi - \sum_{i=2}^{m} i\alpha_i\right), \alpha_2, \ldots, \alpha_m} \times \prod_{i=2}^{m} K_i^{\alpha_i}\right] = \xi K_\xi \quad (12)$$

Then eq 12 can be used immediately to derive explicit expressions to calculate the equilibrium constants, K_ξ, with $\xi = 1, 2, \ldots, m$, for any ideal self-associating system from which values of M_{zc} are available. For this purpose, the values of $\alpha_1, \alpha_2, \alpha_3, \ldots, \alpha_m$ must be calculated such that conditions 1, 2, and 3 (see eq 9) are satisfied in all cases. Since these values are the same as those calculated before (Derechin, 1968) for $\xi = 1, 2, 3$, and 4, those latter values will be used.

Derivation of K_1. The only case is $\xi = 1$, $r = 1$. In this case, $\alpha_1 = 1$, $\alpha_i = 0$, $i > 1$. Using these values, eq 12 can be written as

$$\left(\frac{M_z}{M_1}\right)_{c=0}\left[\frac{1}{1!0!0!\ldots0!}\right]K_2^{\,0}K_3^{\,0}K_4^{\,0}\ldots = 1K_1 = 1 \quad (13)$$

Equation 13 shows that at $c = 0$, $M_z = M_1$.

Derivation of K_2. For $\xi = 2$ and $r = 1$, $\alpha_2 = 1$, $\alpha_i = 0$, $i \neq 2$, and for $\xi = 2$ and $r = 2$, $\alpha_1 = 2$, $\alpha_i = 0, i > 1$. Thus, two summation terms are obtained and eq 12 can be written as

$$2K_2 = K_2 + \frac{1}{2}\left(\frac{\mathrm{d}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c}\right)_{c=0} \quad (14a)$$

and solving for K_2, we have

$$K_2 = \frac{1}{2}\left(\frac{\mathrm{d}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c}\right)_{c=0} \quad (14)$$

Derivation of K_3. For $\xi = 3$ and $r = 1$, a first summation term is obtained with $\alpha_3 = 1$, $\alpha_i = 0$, $i \neq 3$; for $\xi = 3$ and $r = 2$ a second term results with $\alpha_1 = 1$, $\alpha_2 = 1$, $\alpha_i = 0$, $i > 2$. Finally, for $\xi = 3$ and $r = 3$, another term can be written using $\alpha_1 = 3$, $\alpha_i = 0$, $i > 1$. Then, eq 12 can be written as

$$3K_3 = K_3 + K_2\left(\frac{\mathrm{d}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c}\right)_{c=0} + \frac{1}{6}\left(\frac{\mathrm{d}^{(2)}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c^2}\right)_{c=0} \tag{15a}$$

Solving for K_3 and using eq 14, we have

$$K_3 = \frac{1}{4}\left(\frac{\mathrm{d}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c}\right)^2_{c=0} + \frac{1}{12}\left(\frac{\mathrm{d}^{(2)}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c^2}\right)_{c=0} \tag{15}$$

Derivation of K_4. Five summation result with $\xi = 4$. The values of $\alpha_1, \alpha_2, \ldots, \alpha_m$ that satisfy conditions 1, 2, and 3 for each value of r are with $r = 1, \alpha_4 = 1$, $\alpha_i = 0$, $i \neq 4$; with $r = 2$, (a) $\alpha_1 = 1$, $\alpha_2 = 0$, $\alpha_3 = 1$, $\alpha_i = 0$, $i > 3$; and (b) $\alpha_1 = 0$, $\alpha_2 = 2$, $\alpha_i = 0$, $i > 2$; with $r = 3$, $\alpha_1 = 2$, $\alpha_2 = 1$, $\alpha_i = 0$, $i > 2$; and with $r = 4$, $\alpha_1 = 4$, $\alpha_i = 0$, $i > 1$. When all summation terms obtained for $\xi = 4$ are added, eq 12 can be written

$$4K_4 = K_4 + K_3\left(\frac{\mathrm{d}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c}\right)_{c=0} + \tfrac{1}{2}K_2^2\left(\frac{\mathrm{d}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c}\right)_{c=0} + \tfrac{1}{2}K_2\left(\frac{\mathrm{d}^{(2)}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c^2}\right)_{c=0} + \frac{1}{24}\left(\frac{\mathrm{d}^{(3)}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c^3}\right)_{c=0} \tag{16a}$$

Solving for K_4 and using eq 14 and 15 we have

$$K_4 = \frac{1}{8}\left(\frac{\mathrm{d}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c}\right)^3_{c=0} + \frac{1}{9}\left(\frac{\mathrm{d}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c}\right)_{c=0} \times \left(\frac{\mathrm{d}^{(2)}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c^2}\right)_{c=0} + \frac{1}{72}\left(\frac{\mathrm{d}^{(3)}\left(\frac{M_z}{M_1}\right)}{\mathrm{d}c^3}\right)_{c=0} \tag{16}$$

Discussion

The general virtues and disadvantages of the theory here presented are the same already described before (Derechin, 1968) for use with the number- and weight-average molecular weight and will not be repeated here. It must be noted, however, that although the present work also makes use of the multinomial theorem, the derivations here are not functionally related to those obtained in the previous paper and represent an independent method.

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