interdependent. In the present case, it has been found that the amino acid composition of phosphomannans varied both as a function of molecular weight and of phosphate content. A similar observation was made with *S. cerevisiae* mannan by Jones (1968). The amino acid sequence of the protein moiety may determine where the mannan of a particular molecular weight and charge is placed in the cell wall. Thus, mannans could have different structures at bud scars or at different levels within the cell wall. An important observation of the current investigation is that the molecular weight distribution of the phosphomannans varied with the growth phase of the cell. In stationary-phase cells, the phosphomannan low in phosphate content was not cross-linked by protein (mol wt 25,000), while the phosphomannan with a high phosphate content contained a greater proportion of the larger complex (mol wt 500,000). This may indicate that a different population of mannans is formed as the cell ages and the wall performs a new set of functions. Significant changes in the nature of the phosphomannan might also result from changes in the phosphate content of the medium which occur during cell growth (Slodki *et al.*, 1970).

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Equations for the Equilibrium Constants of Nonideal Systems Derived from the Multinomial Theory Using the z-Average Molecular Weight†

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ABSTRACT: Equations for the calculation of equilibrium constant of self-associating systems are derived using $M_{z,app}$.

Equations for the calculation of mass equilibrium constants of self-association reactions for ideal systems using the z-average molecular weight were given before (Derechin, 1969b). In this paper equations for nonideal systems using the z-average molecular weight are derived.

Theory

Various definitions and derivations made before for ideal systems (eq 4–11 of paper III of this series, Derechin, 1969b) can be applied to nonideal systems simply by replacing $M_{z,app}$ for M_z thus leading to eq 1, where $M_{z,app}$ is the z-average molecular weight as calculated from experimental data.

$$\sum_{r=1}^{\xi}\left(\frac{d^{(r-1)}\frac{M_{z,app}}{M_1}}{dc^{r-1}}\right)_{c=0}\times\left[\sum_{\alpha_2=0}^{r}\cdots\sum_{\alpha_m=0}^{r}{}_{(\alpha_1,\,\alpha_2,\,\ldots,\,\alpha_m)}{}^{1}\prod_{i=2}^{m}K_i^{\alpha i}\right]=\xi K_\xi \quad (1)$$

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$M_{z,app}(c)$ differs from $M_z(c)$ as shown by eq 2a (Adams

$$M_{z,app}(c) = M_z(c)/(1 + BcM_w(c))^2 \quad (2a)$$

and Filmer, 1966), where B is the virial coefficient, c, is the concentration in g/100 ml, and $M_w(c)$ is the weight-average molecular weight. $M_{z,app}(c)$ can be calculated from experiments that supply $M_{w,app}(c)$ using eq 3 (Adams, 1962; Adams and Filmer, 1966).

$$M_{z,app}(c) = \frac{d}{dc} cM_{w,app}(c) \quad (3)$$

Equations for the equilibrium constants for the nonideal case could be obtained after differentiating eq 2a and then replacing these results into eq 1. However, an equivalent but simpler procedure is to solve eq 2a for $M_z(c)$ (eq 2) then cal-

$$M_z(c) = M_{z,app}(c) + 2M_{z,app}(c)M_w(c)Bc + M_{z,app}(c)M_w(c)^2B^2c^2 \quad (2)$$

culate the various $(d^{(r)}M_z/dc^r)_{c=0}$, where $r = 1, 2, \ldots$, and finally replace these derivatives into the already derived equations for the ideal case (eq 13–16 of paper III of this series, Derechin, 1969b).

The calculation of the successive $(d^{(r)}M_z/dc^r)_{c=0}$ require expressions for the successive $(d^{(r)}M_w/dc^r)_{c=0}$. These can be calculated after putting the definition of $M_{w,app}(c)$ (Adams and Fujita, 1963) in the form of eq 4. Thus, the derivatives of

$$M_w(c) = M_{w,app}(c)/(1 - M_{w,app}Bc) \quad (4)$$

M_w and M_z, respectively, needed for the calculation of K_2, K_3, and K_4 are

$$\left(\frac{d^{(1)}M_w}{dc}\right)_{c=0} = \left(\frac{d^{(1)}M_{w,app}}{dc}\right)_{c=0} + M_1X \quad (5)$$

$$\left(\frac{d^{(2)}M_w}{dc^2}\right)_{c=0} = 2M_1X^2 + 4\left(\frac{d^{(1)}M_{w,app}}{dc}\right)_{c=0} X + \left(\frac{d^{(2)}M_{w,app}}{dc^2}\right)_{c=0} \quad (5a)$$

$$\left(\frac{d^{(1)}M_z}{dc}\right)_{c=0} = \left(\frac{d^{(1)}M_{z,app}}{dc}\right)_{c=0} + 2M_1X \quad (6)$$

$$\left(\frac{d^{(2)}M_z}{dc^2}\right)_{c=0} = \left(\frac{d^{(2)}M_{z,app}}{dc^2}\right)_{c=0} + 6\left(\frac{d^{(1)}M_{z,app}}{dc}\right)_{c=0} X + 6M_1X^2 \quad (6a)$$

$$\left(\frac{d^{(3)}M_z}{dc^3}\right)_{c=0} = 24M_1X^3 + 36\left(\frac{d^{(1)}M_{z,app}}{dc}\right)_{c=0} X^2 + \left[8\left(\frac{d^{(2)}M_{z,app}}{dc^2}\right)_{c=0} + \frac{6}{M_1}\left(\frac{d^{(1)}M_{z,app}}{dc}\right)^2_{c=0}\right] X + \left(\frac{d^{(3)}M_{z,app}}{dc^3}\right)_{c=0} \quad (6b)$$

where $X = BM_1$. After replacing eq 5–6 into the equations for the ideal case (Derechin, 1969b) we obtain the equations for the nonideal case

$$K_2 = X + \frac{1}{2}ma \quad (7)$$

$$K_3 = \frac{3}{2}X^2 + \frac{3}{2}maX + \frac{1}{4}m^2a^2 + \frac{1}{12}mb \quad (8)$$

$$K_4 = \frac{8}{3}X^3 + 4maX^2 + \left[\frac{3}{2}m^2a^2 + \frac{1}{3}mb\right]X + \frac{1}{8}m^3a^3 + \frac{1}{9}m^2ab + \frac{1}{72}mc \quad (9)$$

where $m = 1/M_1$, and a, b, and c, respectively, are the first, second, and third derivatives of $M_{z,app}$ with respect to c at $c = 0$.

Discussion

Equations for the calculation of equilibrium constants of self-associating systems using $M_{z,app}(c)$ have been presented. These equations have been tested using error-free model systems (computer program LVOUTR3). Also, using experimental data analyzed in a previous paper (Derechin, 1971) the method described here gave similar results. For the analysis of experimental data (computer program MWEXR3), $M_{w,app}$ *vs.* c, these are converted into a table of $M_{z,app}$ *vs.* c using eq 3. This procedure makes the method dependent on the availability of suitable data from sedimentation equilibrium experiments. Thus, the discussion made before (Derechin, 1971) on criteria and procedure for the selection of data can be extended to the present case. It must be noted here that plots of $(1/r)(dc/dr)$ *vs.* c. (Van Holde and Baldwin, 1958) also lead to the calculation of $M_{z,app}$ from experiment. Although the method of Van Holde *et al.* (1958), as described by these authors, permits the calculations of a molecular weight-average throughout the cell, the analysis of data $(1/r) \times (dc/dr)$ and $c(r)$ should supply $M_{z,app}(c)$. Although we have not done experiments in this manner it appears worthwhile exploring this method since in some laboratories only schlieren optics is in use. Then, if reliable data, $M_{z,app}(c)$ are available, the polynomial regression of these data may permit the calculation of the equilibrium constants by the method described here.

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