0.671, 0.75, 0.8, etc. if the graphs are assumed to be strictly linear. Where narrower distributions are encountered, the exponent α (see the Appendix) becomes less than $\frac{1}{2}$ and such distributions may more readily be characterized by linearity of the appropriate plot, because the smaller the exponent the less serious is the assumption that $\int (\int_{\xi}^{\infty} c d\xi) d\xi$ is 0 at $\xi = 1$. For example, with a Schulz distribution having $h = 2$, $c^{-\frac{1}{2}}$ is linear with ξ to a high degree of accuracy if $c_m < 10^{-3} \times c_b$.

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APPENDIX

Derivation of an Approximate Function Relating c and ξ for Schulz Molecular-Weight Distributions in the Meniscus-Depletion Condition in the Equilibrium Ultracentrifuge

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Most-Probable Case

With the notation from Table 1 of the main paper (Gibbons *et al.*, 1973), successive molecular-weight averages may be written (Fujita, 1962):

$$M_n = \frac{c_o \lambda}{\left[\int_0^1 \left(\int_{\xi}^{\infty} c d\xi \right) d\xi \right]} \quad (1)$$

$$M_w = \frac{1}{\lambda c_o} (c_b - c_m) \quad (2)$$

$$M_z = \frac{1}{\lambda^2 c_o M_w} \left[\left(\frac{dc}{d\xi} \right)_m - \left(\frac{dc}{d\xi} \right)_b \right] \quad (3)$$

and generally:

$$M_{(z+n)} = \frac{1}{\lambda^{(n+2)} c_o M_w M_z \dots M_{(z+n-1)}} \times \left[\left(\frac{d^{(n+1)}c}{d\xi^{(n+1)}} \right)_m - \left(\frac{d^{(n+1)}c}{d\xi^{(n+1)}} \right)_b \right] \quad (4)$$

if n is an even integer; if it is odd then the term within the square brackets becomes

$$\left[\left(\frac{d^{(n+1)}c}{d\xi^{(n+1)}} \right)_b - \left(\frac{d^{(n+1)}c}{d\xi^{(n+1)}} \right)_m \right]$$

The ratios of successive molecular-weight averages simplify to

$$\frac{M_n}{M_w} = \frac{c_o^2}{\left[\int_0^1 \left(\int_{\xi}^{\infty} c d\xi \right) d\xi \right] (c_b - c_m)} \quad (5)$$

$$\frac{M_w}{M_z} = \frac{(c_b - c_m)^2}{c_o \left[\left(\frac{dc}{d\xi} \right)_m - \left(\frac{dc}{d\xi} \right)_b \right]} \quad (6)$$

$$\frac{M_z}{M_{(z+1)}} = \frac{\left[\left(\frac{dc}{d\xi} \right)_m - \left(\frac{dc}{d\xi} \right)_b \right]^2}{(c_b - c_m) \left[\left(\frac{d^2c}{d\xi^2} \right)_b - \left(\frac{d^2c}{d\xi^2} \right)_m \right]}$$

and generally:

$$\frac{M_{(z+n-1)}}{M_{(z+n)}} = \frac{\left[\left(\frac{d^n c}{d\xi^n} \right)_m - \left(\frac{d^n c}{d\xi^n} \right)_b \right]^2}{\left[\left(\frac{d^{(n-1)}c}{d\xi^{(n-1)}} \right)_m - \left(\frac{d^{(n-1)}c}{d\xi^{(n-1)}} \right)_b \right] \left[\left(\frac{d^{(n+1)}c}{d\xi^{(n+1)}} \right)_m - \left(\frac{d^{(n+1)}c}{d\xi^{(n+1)}} \right)_b \right]} \quad (7)$$

The numerator and denominator of the right-hand side of eqn. (7) are both products of quantities of like sign: notwithstanding the alternation in sign which occurs with parity in eqn. (4), eqn. (7) as written is therefore always positive.

For the most-probable distribution of molecular weights it is required that eqns. (5), (6) and (7) should have the values $\frac{1}{2}$, $\frac{2}{3}$ and $(n+2)/(n+3)$ respectively. That is, c must be written as some function of ξ such that successive differentiation of it will always reduce eqn. (7) to $(n+2)/(n+3)$ where n is the number of times the operation of differentiation has been carried out. If M_w is considered to be $M_{(z-1)}$ and M_n to be $M_{(z-2)}$, and if the operator $d^n c/d\xi^n$ is defined for $n = -1$ and -2 as well as for $0, 1, 2, \dots$, that is, negative-order differentials are taken to represent the integrations performed explicitly in eqn. (5), then eqn. (7) may be considered to have complete generality. This is convenient because it is easier to look for a function that will represent the double integral in eqn. (5) and can be differentiated twice to obtain c as a function of ξ rather than search for a function that can be integrated to give the appropriate values to eqns. (5) and (6).

This problem is greatly simplified if the high-speed meniscus-depletion experiment is considered. In this condition c_m and its derivatives with respect to ξ are small compared with the same quantities at the base of the cell. If all m -subscripted variables are equated to zero, eqn. (7) simplifies:

$$\frac{M_{(z+n-1)}}{M_{(z+n)}} = \frac{\left(\frac{d^n c}{d\xi^n} \right)_b^2}{\left(\frac{d^{(n-1)}c}{d\xi^{(n-1)}} \right)_b \left(\frac{d^{(n+1)}c}{d\xi^{(n+1)}} \right)_b} \quad (8)$$

Evidently a function is sought of which the derivative can be expressed to any order and which, when

inserted into the right-hand side of eqn. (8) will give $(n+2)/(n+3)$ for all integral values of n greater than -1 , including 0 . Following the convention given regarding the operator $d^n c/d\xi^n$ for negative values of n and inspecting the functions listed by Kynch (1955) as having an indefinite series of higher derivatives, it can be seen that putting $d^{-2}c/d\xi^{-2} = 1/(q\xi + k)$ will give the required solutions to eqn. (8). This implies that:

$$c = 2q^2/(q\xi + k)^3 \quad (9)$$

The general expression for $d^n c/d\xi^n$ now becomes $(n+2)!q^{(n+2)}/(q\xi + k)^{(n+3)}$. Substituting in eqn. (8):

$$\frac{M_{(z+n-1)}}{M_{(z+n)}} = \frac{\left[\frac{(n+2)! q^{(n+2)-2}}{(q+k)^{(n+3)}} \right]}{\left[\frac{(n+1)! q^{(n+1)}}{(q+k)^{(n+2)}} \right] \left[\frac{(n+3)! q^{(n+3)}}{(q+k)^{(n+4)}} \right]}$$

$$= \frac{[(n+2)!]^2}{(n+1)!(n+3)!} = \frac{n+2}{n+3}$$

Given that the approximation in simplifying eqn. (7) to eqn. (8) is justified in the experimental conditions prevailing, then eqn. (9) satisfies the condition for the concentration distribution at equilibrium for a polydisperse material having the most-probable distribution of molecular-weight averages. Its point value at $\xi = 0$ and all its derivatives to infinity at that point fulfil the requirements for the values to be taken by eqn. (8). Under these circumstances $c^{-\frac{1}{3}}$ will be linear with ξ , the line having slope $(q/2)^{\frac{1}{3}}$ and intercept $k/q^{\frac{2}{3}}$. The quantities k and q are thus seen to be experimental constants depending upon c_o and ω ; moreover

$$M_{(z+n)} = \frac{(3+n)}{\lambda} \cdot \frac{q}{k} = \frac{(3+n)}{\lambda} \cdot \frac{\text{slope}}{\text{intercept}}$$

Recalling that putting $n = -2$ and -1 generates M_n and M_w respectively, all molecular-weight averages become available from a plot of $c^{-\frac{1}{3}}$ against ξ .

General Case

Schulz distributions are represented by:

$$f(M) = \frac{p^{(h+1)}}{\Gamma(h+1)} M^h e^{-pM} \quad (10)$$

where Γ is the gamma function and p and h are two adjustable parameters of which h uniquely defines the width of the distribution as it is evidenced in the ratios of successive molecular weights. These ratios become $M_n/M_w = h/(h+1)$, $M_w/M_z = (h+1)/(h+2)$, and generally, $M_{(z+n)}/M_{(z+n+1)} = (h+n+2)/(h+n+3)$; the analysis for the most probable case is thus a special case in which $h = 1$. The function $1/(q\xi + k)^h$

may be differentiated indefinitely even when $h \neq 1$, provided h is positive, giving, generally:

$$\frac{d^n c}{d\xi^n} = \frac{q^n \prod_{i=1}^{i=n} (i+h-1)}{(q\xi+k)^{(h+n)}} \quad (11)$$

By applying the same reasoning as that for the most-probable case we may write:

$$c = \frac{q^2 h(h+1)}{(q\xi+k)^{(h+2)}} \quad (12)$$

Thus generally $c^{-\alpha}$ becomes linear with ξ where $\alpha = 1/(h+2)$. Where $0 < h < 1$ the distribution is broader than the one for the most-probable distribution and where $h > 1$ it is sharper; h must be finite and positive, thus the exponent $(h+2)$ in eqn. (12) cannot be less than 2 for the Schulz distribution eqn. (10) to hold.

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