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MOLAR MASS DETERMINATION FROM SEDIMENTATION DIFFUSION EQUILIBRIUM

With moderate rotor speed at sufficiently long run time of the centrifuge an equilibrium between sedimentation and back-diffusion of the dissolved macromolecules is reached. One distinguishes between "high speed" or "meniscus depletion" equilibrium, where the polymer concentration at the meniscus comes to zero, and "low speed" equilibrium (Fig. 1) which is more adequate for samples with broad mass distribution. From the equilibrium concentration distribution between cell meniscus and bottom which is detected by UV-absorbance or interference optics the average molar masses M_W (weight average) and M_z (centrifuge average) can be calculated after an appropriate extrapolation to zero concentration (Fig. 2).

$$M_{w,app} = \frac{c_b - c_m}{\lambda c_o}$$

$$M_{z,app} = \frac{c_b (d\ln c/dx)_b - c_m (d\ln c/dx)_m}{\lambda (c_b - c_m)}$$

with

$$\lambda = (1-\bar{v}\rho_o)\cdot\omega^2\cdot(r_b^2 - r_m^2)/2RT$$

and extrapolation to $c_0 = 0$ according to

$$\frac{1}{M_{app}} = \frac{1}{M} + B\cdot c_o$$

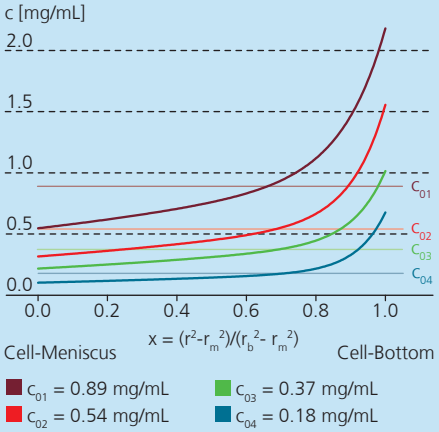

Fig. 1 Concentration distribution at „low speed" sedimentation equilibrium.

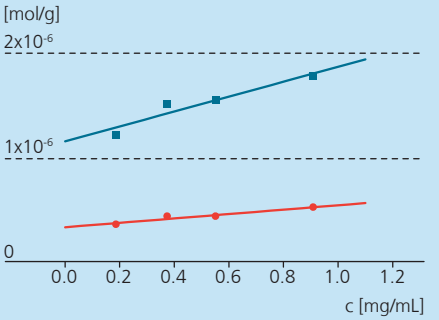

Fig. 2 Extrapolation of the apparent molar masses to c=0.

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