Fraunhofer Institut Angewandte Polymerforschung

Molar mass determination from sedimentation diffusion equilibrium

With moderate rotor speed at sufficient 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 (Figure 1) which is more adequate for samples with broad mass distribution.

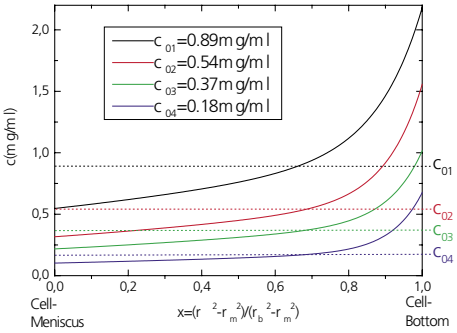

Figure 1
Concentration distribution at „low speed" sedimentation equilibrium

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 (Figure 2).

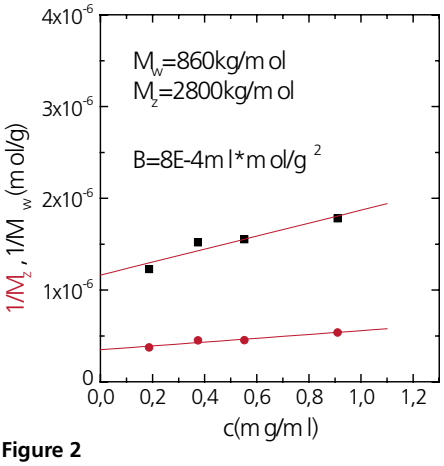

Figure 2
Extrapolation of the apparent molar masses to c=0

$$M_{w,app} = \frac{c_b - c_m}{\lambda\, c_0}$$

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

with

$$\lambda = (1 - \bar{\nu}\rho_0) \cdot \omega^2 \cdot (r_b^2 - r_m^2) / 2RT$$

and extrapolation to $c_0 = 0$ according to

$$\frac{1}{M_{app}} = \frac{1}{M} + B \cdot c_0$$

Fraunhofer-Institut für Angewandte Polymerforschung
Wissenschaftspark Golm
Geiselbergstraße 69
14476 Potsdam
Germany

Phone +49(0)331/568-10
Fax +49(0)331/568-3000
E-mail info@iap.fraunhofer.de
www.iap.fraunhofer.de

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