Molecular Weight Measurement of Polystyrene by Archibald Method

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Archibald[1] and others[2-9] have reported a method of determining molecular weight by ultracentrifuge during approach to sedimentation equilibrium. Application of this method to synthetic high polymer has been studied in this experiment.

Polystyrene which was used as the common sample by the research group of light scattering measurement in Japan was centrifuged with two kinds of ultracentrifuge, the magnetically suspended free running type ultracentrifuge with a Rayleigh interference optical system and a Spinco Model E ultracentrifuge with a schlieren optical system. All this experiments were done in butanone solution.

Weight average molecular weight, M_w, in this method is determined by obtaining the quantity δ_w at the point a and b, the boundary surface of solution and the bottom of cell, according to the following equation.

$$\delta_w = (1/xC)(dC/dx) = (1-\bar{v}\rho)\omega^2 M_w/RT \quad (1)$$

where x is the distance from the center of rotation, C the concentration of solution, $\bar{v}$ the partial specific volume of solute, ρ the density of solution, R the gas constant, T the absolute temperature, and ω the angular velocity of rotation.

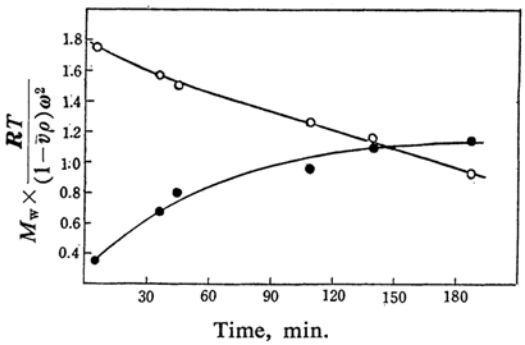

Fig. 1. Time dependencies of the apparent average molecular weights, M_{wb} and M_{wa}, calculated by Archibald's equation.
$C_0 = 0.243$ RPM $= 7.6 \times 10^3$
● δ_{wa} ○ δ_{wb}

The values of δ_{wa} and δ_{wb} calculated by Eq. 1 vary with time as shown in Fig. 1. In Archbald's expectation, the curve of δ_{wb} will be higher than that of δ_{wa} and both curves should meet when extrapolated to zero time. To the contrary of expectation, however, δ_{wa}'s are larger than δ_{wb}'s at the initial stage of sedimentation. Thereafter δ_{wa}'s decrease and δ_{wb}'s increase gradually with time and both curves become crossing together after some minutes.

Comparing the results of the free running type ultracentrifuge experiments and those of Spinco ultracentrifuge, this crossing point, t_c, seems to be dependent on the time consumed during driving the rotor to experimental speed. On the other hand, in the results obtained by the later experiment it shows that the other experimental conditions, concentratin of solution and the rotor speed, have the effects on t_c. Trautman plot[8] was also examined.

But the both plots corresponding to the boundary surface of solution and the bottom of cell have curvatures indicating the molecular weight heterogeneity and thermodynamical non-ideality of the solution, and they do not meet at zero time.

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7) H. Fujita et al., *J. Phys. Chem.*, **66**, 4 (1962).
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TABLE I. RESULTS WITH FREE RUNNING TYPE U. C. at 30°C

C_0 g./100 ml.	RPM $\times 10^{-3}$	t_c min.	M_w^{app} $\times 10^{-4}$	M_w^{app}* $\times 10^{-4}$
0.120	5.4	135	29.6	23.0
0.222	5.8	285	23.1	19.5
0.411	5.7	225	20.9	17.8
0.694	5.8	195	19.3	15.8
$C_0 \rightarrow 0$	—	—	31.2	26.4

* The results obtained by sedimentation equilibrium.

TABLE II. RESULTS WITH SPINCO MODEL E U. C. at 20°C

C_0 g./100 ml.	RPM $\times 10^{-3}$	t_c min.	M_w^{app} $\times 10^{-4}$
0.137	10.5	7	20.5
0.209	10.5	12	17.7
0.384	10.5	13	15.4
0.242	8.7	15	17.9
0.242	7.2	18	17.6
0.242	5.1	32	17.0
$C_0 \rightarrow 0$	—	—	23.0

This abnormality is resulted in all our experiments. Then we assumed the values at t_c as δ_w's of the whole solute, and calculated the hypothetical apparent weight average molecular weight, M_w^{app}. The reciprocals of these M_w^{app}'s were plotted against concentration and extrapolated to infinite dilution. The results obtained are shown in Tables I and II with the values obtained by sedimentation equilibrium.

It may be concluded from the results that the Archibald method is a rapid and useful technique in molecular weight measurement but it has some ambiguities in the determination of the average molecular weight of the whole solute which has a molecular weight distribution.

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