

Sedimentation in dilute polystyrene–cyclohexane solutions close to the theta temperature

C. Destor and F. Rondelez

Collège de France, Physique de la matière condensée, 11 Place Marcellin-Berthelot, 75231 Paris Cédex 05, France

(Received 19 February 1980)

Sedimentation velocity measurements have been performed on polystyrene–cyclohexane solutions close to the theta-temperature. Contrary to previous reports, the sedimentation coefficient s is not dependent on the velocity of the rotor when the data are extrapolated to atmospheric pressure. The pressure dependence of s has been measured to be $\mu \approx 1.7 \times 10^{-8} \text{ Pa}^{-1}$. This is not an anomalous result for polymer solutions, since similar results have been reported for polyisobutylene chains dissolved in a good solvent, n-octane.

INTRODUCTION

Sedimentation velocity measurements of dilute polymer solutions close to the theta temperature have been a matter of controversy for many years. Conflicting results have been published on an anomalous dependence of the sedimentation coefficient on the rotor speed. This dependence was reported to be strong by Jacob *et al.*¹, much weaker by Kotaka and Donkai², and non-existent by Sundelöf and Nyström³, although all the experiments were performed on polystyrene–cyclohexane solutions and over the same range of rotor speed. The necessity of correcting the data for the large hydrostatic pressures generated during a centrifugation run has been pointed out by Kotaka² but refuted by Jacob¹ in his early experiments. Thus it seems important to resume careful sedimentation velocity experiments on the same polymer–solvent system, i.e. dilute solutions of polystyrene–cyclohexane, close to the theta temperature.

EXPERIMENTAL

Experiments were performed in a Spinco model E ultracentrifuge equipped with a schlieren optical system. The runs were made at five different speeds: 51 500; 47 900; 36 000; 25 800; and 19 900 rpm. The error and fluctuations in rotor speed were $\approx 1\text{--}2\%$. An RTIC unit permitted the temperature of the cell to be controlled to within $\pm 0.1^\circ\text{C}$. Two temperatures were used: 35.4°C , close to the theta temperature⁴; and 28.0°C , just above the demixing temperature. The cell was a 12 mm thick, 10 mm long, 4° single sector. The polymer solution was introduced into the cell at high temperature ($\approx 50^\circ\text{C}$) and was then allowed to reach its nominal temperature slowly to ensure good thermodynamic equilibrium.

The sedimentation coefficient was determined from the displacement of the boundary peak over the longest possible distance within the cell in an attempt to maximize the pressure effects exerted by the liquid column between the meniscus and the sedimentation boundary. Up to 60 photographs were taken. They were read with a Zeiss microcomparator capable of a $\pm 2 \mu\text{m}$ resolution. However, the finite width of the schlieren peak limited the overall accuracy to $\pm 10 \mu\text{m}$ ($\pm 5 \mu\text{m}$ on the actual cell

dimension when taking into account the optical magnification of the ultracentrifuge).

A single polymer concentration of $0.25 \times 10^{-2} \text{ g cm}^{-3}$ was used since at the Flory temperature the polymer solution becomes thermodynamically ideal. The concentration dependence of the sedimentation coefficient is then expected to be restricted to hydrodynamic interactions, which are weak for moderate polymer molecular weights⁵. The polystyrene chains used here had a molecular weight of 230 000 and a low polydispersity index M_w/M_n of 1.1. They were purchased from Pressure Chemicals (Pittsburg, Pennsylvania) and used as received. The cyclohexane solvent was spectroscopic grade (Merk–Uvasol).

RESULTS

A typical plot of the peak position r_H versus time is displayed on semilogarithmic axes in Figures 1 and 2 at 35.4°C for two different rotor speeds. At the lowest speed of 25 800 rpm all the data points align on a straight line while they show a marked downwards curvature at 51 500

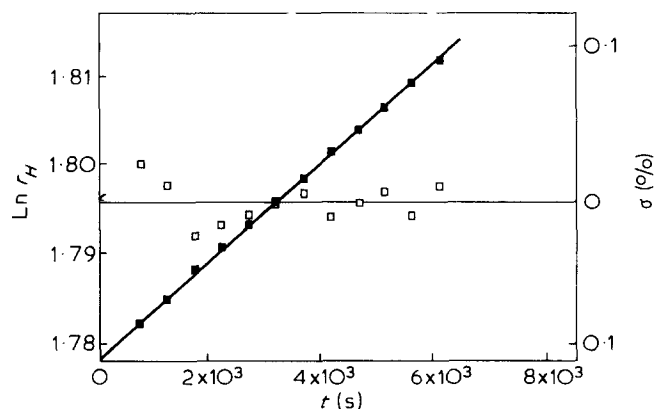


Figure 1 Sedimentation peak position vs. time in semilogarithmic scales (■). The solid line is the calculated best fit to a linear function. The σ points (□) represent the relative deviation between the experimental data points and the calculated values. $T = 35.4^\circ\text{C}$, polymer concentration = $0.25 \times 10^{-2} \text{ g cm}^{-3}$, rotor speed = 25 800 rpm

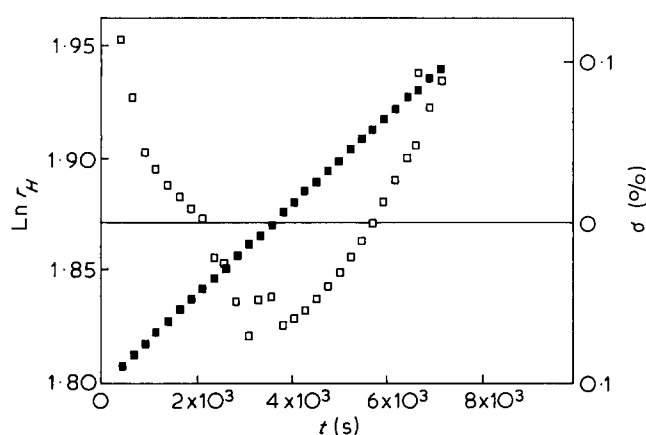


Figure 2 Same as Figure 1 but rotor speed = 51 500 rpm. For sake of clarity the solid line corresponding to the best fit to a linear function has not been drawn explicitly

rpm. More quantitatively, if we perform a least-squares fit with a linear function:

$$y_{\text{calc}} = (\ln r_H)_{\text{calc}} = At + B$$

we obtain an excellent quality factor⁶ of 0.84 in the first case and a poor one of 0.12 in the second case. This difference is well reflected by the relative deviation σ between the calculated best fit, y_{calc} , and the experimental values y_{exp} :

$$\sigma = \frac{y_{\text{exp}} - y_{\text{calc}}}{y_{\text{calc}}}$$

σ never exceeds 0.02% for the low speed data of Figure 1 but is of the order of 0.1% for most of the high speed data of Figure 2. In this latter case, the fit is much better if we use a quadratic function in time:

$$y_{\text{calc}} = (\ln r_H)_{\text{calc}} = At^2 + Bt + C$$

The quality factor rises to 0.96 and σ falls by nearly one order of magnitude from 0.1% to 0.02%. This is indicated in Figure 3 where the calculated curve has been drawn as a solid line.

It is possible to calculate the sedimentation coefficient s from the data given in Figures 1 and 2. By definition, s is written as:

$$s = \frac{1}{\omega^2} \left(\frac{d \ln r_H}{dt} \right)$$

where ω is the angular velocity of the rotor. In simple cases where r_H increases linearly with time, s is independent of the peak position. From the slope of the curve shown in Figure 1, we obtain $s = 7.4 \pm 0.2$ S at 25 800 rpm where S stands for the Svedberg unit = 10^{-13} s. However, in more complicated cases, we have to take the local derivative at each point and s is no longer independent of peak position within the cell. For the quadratic polynomial fit in Figure 3, s varies from 7.3 ± 0.2 S at the meniscus to 6.1 ± 0.2 S close to the bottom of the cell, at 51 500 rpm. Additional runs made at 36 000 rpm show the same effects with s varying from 7.4 ± 0.2 to 6.6 ± 0.2 S.

Experiments at different rotor speeds, 47 900 and 19 900 rpm have also been performed at 28°C, i.e. 7°C below the theta temperature and close to the demixing point: similar

behaviour is again observed. At the highest speed, the experimental points are best fitted by a quadratic law versus time. The calculated values for the sedimentation coefficient yield s values decreasing from 7.1 ± 0.2 to 6.2 ± 0.2 S between the meniscus and the bottom of the cell. At 19 900 rpm, s is constant and equal to 7.3 ± 0.2 S.

DISCUSSION

During a centrifugal run, high hydrostatic pressures, P , develop. They are generated in the polymer solution by the liquid column between the meniscus and the solution boundary:

$$P = \frac{1}{2} \rho_0^0 \omega^2 (r_H^2 - r_m^2)$$

where ρ_0^0 is the solvent density at $P=0$ and r_H and r_m are the positions of the solution boundary and solvent meniscus, respectively. The pressure increases as the boundary moves towards the bottom of the cell and this progressively changes the physical parameters of the polymer solution. In general a decrease in s is apparent, but the dilution effect due to the sector shape of the cell tends to increase s .

Experimentally, we observe a decrease in s with boundary position but only at the highest speeds attainable with the ultracentrifuge ($> 36\,000$ rpm). This is strongly suggestive of a pressure effect since this is the condition for maximum hydrostatic pressures.

Assuming negligible diffusion, Fujita⁷ has given a derivation of the Lamm equation which takes into account the effect of pressure and concentration on the sedimentation of polymer solutions. The equation for $\ln r_H$ versus t is:

$$\frac{\ln(r_H/r_m)}{\omega^2 t} = s(c, 0) \left(1 + K \left[\left(\frac{r^2}{r_m^2} \right) - 1 \right] \right) \quad (1)$$

with

$$K = -\frac{m}{2} + \frac{1-m}{2} \frac{kc}{1+kc}$$

and

$$m = \frac{1}{2} \mu \rho_0^0 \omega^2 r_m^2$$

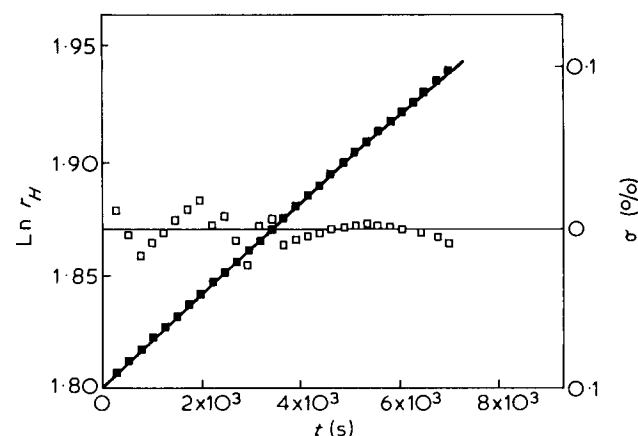


Figure 3 Same data points as in Figure 2 (■). The experimental values have been fitted to a quadratic function of time, represented as a full line. The σ points (□) represent the relative deviation between the experimental data points and the calculated values

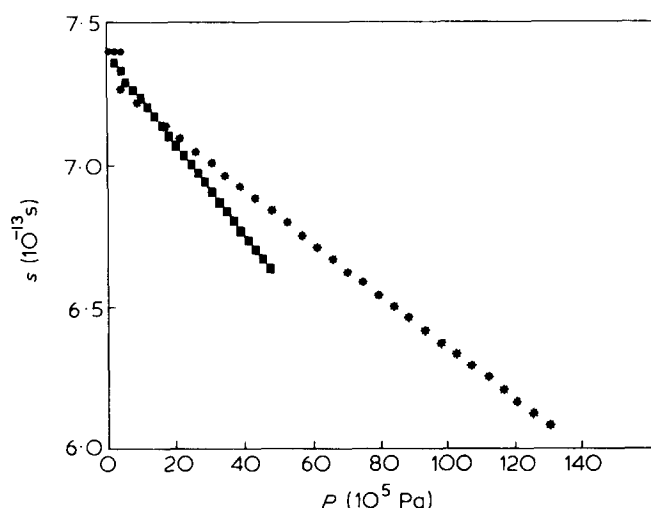


Figure 4 Sedimentation coefficient s versus hydrostatic pressure P induced during centrifugation runs at 3 different rotor speeds: ●, 25 800 rpm; ■, 36 000 rpm; and *, 51 500 rpm. $T = 35.4^\circ\text{C}$

k is a coefficient describing the concentration dependence of the sedimentation coefficient s at atmospheric pressure:

$$s(c, 0) = s(0, 0)(1 + kc)^{-1} \quad (2)$$

and μ is the coefficient describing the pressure dependence of s

$$s(c, P) = s(c, 0)(1 - \mu P) \quad (3)$$

The Fujita method assumes sedimentation over a large distance within the cell. By plotting

$$\ln(r_H/r_m)/\omega^2 t \text{ versus } \frac{r_H^2}{r_m^2} - 1$$

we may deduce $s(c, 0)$ and K from a single run. However, equation (1) requires a precise knowledge of the starting time of the sedimentation run. This is not easy to determine experimentally². We therefore prefer to use a slightly different method which treats the experimental data points directly and yields the zero time naturally.

We first remark that the theta conditions minimize the effects of the concentration dependence of s . Indeed at the theta temperature the polymer chains become ideal and their mutual interactions are very weak for dilute solutions. In our case, kc is estimated to be $\sim 2\%$ if we use the data of ref 3. Therefore the Fujita equation reduces to:

$$\frac{\ln(r_H/r_m)}{\omega^2 t} \approx s(c, 0) \left(1 - \frac{\mu P}{2}\right) \quad (4)$$

By developing the pressure variation *versus* time to first order

$$\ln(r_H/r_m) = s(c, 0)\omega^2 t + At^2 \quad (5)$$

where

$$A = -\frac{1}{2}\mu\rho_0^0\omega^6 s^2(c, 0)r_m^2 \quad (6)$$

Since zero time is not accurately known, we can only

connect the real time t to the experimental time t' by:

$$t = t' + \Delta t$$

where Δt represents the time elapsed between the beginning of the run and the first photograph. If we call r_1 the peak position on the first photograph at time $t' = 0$, we obtain:

$$\ln \frac{r_H}{r_1} = At'^2 + (B + A\Delta t)t' \quad (7)$$

For the run represented in Figure 3:

$$A \approx 10^{-10} \text{ s}^{-2}, \quad B \approx 10^{-5} \text{ s}^{-1} \quad \text{and} \quad t \approx 10^2 \text{ s}$$

so we have $B \gg A\Delta t$. The final result is then:

$$\ln \frac{r_H}{r_1} = At'^2 + Bt' \quad (8)$$

This derivation shows that it is permissible to analyse the experimental data for $\ln r_H$ using quadratic functions of time t' . This also gives support to the assumption that pressure effects can explain the sedimentation behaviour at high rotor speeds.

It is then logical to replot our data of $\ln r_H$ *versus* time as $\ln r_H$ *versus* pressure, calculating the hydrostatic pressure for each position on the boundary peak within the cell. This is done in Figure 4 at 35.4°C and for three different rotor speeds. At the lowest speed, 25 800 rpm, the induced pressure is too small to allow for a detectable change in s . At the two highest speeds of 36 000 and 51 500 rpm, s is observed to decrease linearly with pressure. This is in agreement with equation (3). From the slope of the two curves, we obtain:

$$\mu = 2.3 \times 10^{-8} \text{ Pa}^{-1} \text{ at } 36\,000 \text{ rpm}$$

$$\mu = 1.3 \times 10^{-8} \text{ Pa}^{-1} \text{ at } 51\,500 \text{ rpm}$$

At 28°C the same data analysis gives a similar value for μ

$$\mu \approx 1.6 \times 10^{-8} \text{ Pa}^{-1} \text{ at } 47\,900 \text{ rpm}$$

while no value can be derived at 19 800 rpm since the pressure variation during the centrifugation run is limited to $5 \times 10^5 \text{ Pa}$.

It is surprising to observe different values of μ depending on rotor speed. Literature data for the same polymer-solvent system also seem to vary between 1.2 and $2.0 \times 10^{-8} \text{ Pa}^{-1}$ ^{2,8}. This may be due to the uncertainty in rotor speed measurements since even a slight error in ω leads to huge variation in μ . Equation (6) yields:

$$\frac{\Delta\mu}{\mu} = \frac{6\Delta\omega}{\omega}$$

Calculations from independent physical data for the cyclohexane-solvent give $\mu = 2.0 \times 10^{-8} \text{ Pa}^{-1}$.

An important point is to check that the extrapolation to atmospheric pressure leads in all runs to the same $s(c, 0)$ value whatever the rotor speed is. By definition, $s(c, 0)$ has to be independent of the experimental conditions. In Figure 4 we observe that this is indeed the case. Within

experimental accuracy one obtains for the three different speeds:

$$s(c, 0) = 7.3 \pm 0.2 \text{ S}$$

This value is in good agreement with the generally accepted law for polymer chains at the theta temperature.

$$s(0, 0) = K_s M_w^{1/2}$$

Taking $K_s = (1.5 \pm 0.2) \times 10^{-15}$ as derived experimentally by various authors^{2,8,9}, we obtain for $M_w = 230\,000$:

$$s(0, 0) = 7.2 \pm 0.9 \text{ S}$$

At 28°C, the s data all extrapolate to the same $s(c, 0)$ value, namely $s(c, 0) = 7.2 \pm 0.2 \text{ S}$.

It is remarkable that the two $s(c, 0)$ values at 28° and 35.4°C are equal within experimental error. This rules out the possibility of an indirect s dependence on pressure via a rise of the theta point. Indeed the upper critical consolute temperature T_c increases with pressure. Typical values $\Delta T_c / \Delta P \approx 2 \times 10^{-8} \text{ °C Pa}^{-1}$ have been reported in the literature for polystyrene-cyclohexane solutions with similar molecular weights¹⁰. Assuming a similar variation for the theta temperature, we can thus expect a 0.3°C increase of the theta point at the highest induced pressure of $1.5 \times 10^7 \text{ Pa}$. For a solution kept at fixed temperature, this effect certainly changes the solvent quality and brings the system closer to the demixing point. However, it is clear that this cannot explain our observations since a 7°C variation from 35.4°C down to 28°C in two separate experiments shows no difference in the absolute values of s .

CONCLUSION

Our experiments confirm and extend the earlier results of Donkai *et al.*² in the polystyrene-cyclohexane system.

The pressure dependence of the sedimentation coefficient is not negligible ($\approx 2\%$ for 10^6 Pa and 230 000 molecular weight) and has to be accounted for in accurate measurements. However, we do not obtain the huge variations ($\approx 20\%$) observed by Jacob *et al.*¹. We do not believe that the vicinity of the theta temperature creates any peculiarity in the sedimentation behaviour. Effects of the same magnitude have been observed in other polymer-solvent systems, especially with good solvents¹¹. Our experiments at two different temperatures show that the main influence of the pressure is on the physical parameters of the solution (friction coefficient, polymer specific volume, solvent density) and not on the thermodynamic solvent quality.

ACKNOWLEDGEMENTS

This research project was supported in part by the French DGRST under Contract No. 77.7.1459. It is our pleasure to thank D. S. Cannell for helpful discussions.

REFERENCES

- 1 Jacob, M., Varoqui, R., Klenine, S. and Daune, M. *J. Chim. Phys.* 1962, **59**, 865
- 2 Kotaka, T. and Donkai, N. *J. Polymer Sci. (A-2)* 1968, **6**, 1457
- 3 Sundelöf, L. O. and Nyström B. *Chem. Scripta*, to be published
- 4 Krigbaum, W. R. and Carpenter, D. K. *J. Phys. Chem.* 1955, **59**, 1166
- 5 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971
- 6 Tournarie, M. *J. Physique (Paris)* 1969, **30**, 47
- 7 Fujita, H. 'The Mathematical Theory of Sedimentation Analysis', Academic Press, New York, 1962
- 8 Billick, I. H. *J. Phys. Chem.* 1962, **66**, 1941
- 9 Homma, T., Kawahana, K., Fujita, H. and Ueda, M. *Makromol. Chem.* 1963, **67**, 132
- 10 Sacki, S., Kuwahana, N., Nakata, M. and Kaneko, M. *Polymer* 1975, **16**, 445
- 11 Nyström, B., Porsch, B. and Sundelöf, L. O. *Eur. Polym. J.* 1977, **11**, 683