

Tips & Tricks: GPC/SEC

Temperature Effects in GPC/SEC

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Temperature effects in GPC/SEC are very often misunderstood and discussed without keeping the specialties of GPC/SEC in mind. From a thermodynamic point of view the GPC/SEC separation mechanism is independent of the temperature. Therefore, there is no need to optimize the set-up for many applications with respect to temperature. However, the temperature influences the polymer solubility, the solvent viscosity and, therefore, the column performance. Consequently some applications require better knowledge about the influence of the temperature on these parameters.

Why is the Ideal GPC/SEC Mechanism Temperature Independent?

The selective distribution of an analyte between mobile phase (eluent) and stationary phase (column material) of a chromatographic system is described using the distribution coefficient K_D . K_D is related to the change in Gibbs free energy difference (ΔG°):

$$\ln K_D = -(\Delta G^\circ/RT) \quad [1]$$

with

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad [2]$$

Depending on the conditions, only entropic (S), only enthalpic (H) or both terms influence the separation behaviour.

In GPC/SEC, separation is accomplished with respect to the hydrodynamic volume and directed by conformational changes. In ideal GPC/SEC systems enthalpic interaction can be avoided and ΔH° can be neglected. Therefore, the distribution coefficient can be expressed as:

$$K_D = e^{(T\Delta S/RT)} = e^{(\Delta S/R)} = K_{SEC} \quad [3]$$

This shows that the temperature dependence on K_{SEC} is minimal. Consequently, if the temperature influences the retention in an application, this indicates non-ideal GPC/SEC behaviour. Compared with other separation techniques this behaviour is unique (e.g., in polymer HPLC/LAC, where the distribution

coefficient is mainly dominated by enthalpic interactions.)¹ Therefore, the distribution coefficient can be expressed as:

$$K_D = e^{(-\Delta H/RT)} = K_{LAC} \quad [4]$$

and temperature variations will lead to a change in peak position.

Polymer Solubility (Sample Preparation) and Temperature

Although required for GPC/SEC characterizations, not all polymers can be dissolved and not all solvents are adequate. The general principle *like dissolves like* is also appropriate in the case of polymers. The dissolution of polymers depends not only on their physical properties, but also (amongst others) on molecular weight, crosslinking and crystallinity. As molecular weight increases, the solubility of a polymer decreases. This same behaviour is also noticed as crosslinking degree increases. For crystalline macromolecules the dissolution can be forced if an appropriate solvent

is available or when warming up to temperatures slightly below the crystalline melting point. For example, highly crystalline linear poly(ethylene) (PE) can be dissolved in several solvents (e.g., TCM, DCB) above 100 °C. Crystalline polymers, more polar than PE (e.g., Nylon 6.6), can be dissolved at room temperature in solvents with enough ability to interact, through, for example, hydrogen bonding.

In general dissolution of polymer samples occurs if the Gibbs free energy of dissolution, ΔG , is negative:

$$\Delta G = \Delta H - T\Delta S \quad [5]$$

The entropy of mixing for polymers in solution is, in most cases, positive. If the enthalpy of mixing, ΔH , is negative (net positive attraction for solute-solvent pairs, good solvents), polymers can be dissolved at any temperature. If ΔH is positive, the $T\Delta S$ term influences the process (poor solvent). For high temperatures $T\Delta S$ dominates and can turn ΔG to higher negative values. In this case dissolution can occur. At low temperatures $T\Delta S$ is less dominant and a polymer can not be dissolved.

Good solvents are favoured for GPC/SEC because of two effects:

- In good solvents the polymer coil is more expanded than in poor solvents. In this case, a given polymer shows a much larger hydrodynamic radius R_H and radius of gyration R_G . The solvent conditions will be influenced by the temperature (see Equation 5).
- Finally, in good solvents polymer-packing material interaction will be suppressed, so the true GPC/SEC mechanism can dominate interaction with column material.²

As a rule of thumb the Mark-Houwink coefficient of the polymer/solvent system should be above 0.63.

Column Performance and Temperature

The resolution of a GPC/SEC column is not independent of the temperature. It depends on the expansion of the polymer (solvent quality, see above) and the diffusion. If the temperature increases, the viscosity of the solvent decreases. If the viscosity decreases, the mobility of a polymer in solution increases, due to easier mass transport. In this case the diffusion coefficient of a polymer in solution increases. This relation between molar mass, solvent viscosity and diffusion coefficient D_M of a polymer can be expressed by:³

$$D_M = \frac{RT}{6\pi\eta N_A} \left(\frac{10\pi N_A}{3K} \right) M_v^{\frac{(1+\alpha)}{3}} \quad [6]$$

R = gas constant

T = absolute temperature

η_0 = solvent viscosity

N_A = Avogadro's Number

K, α = Mark-Houwink coefficients

If the diffusion coefficient of a polymer in solution increases, the resulting polymer peaks appear sharper and less broad. The temperature directly influences the resolution of the GPC/SEC column.

The lower the viscosity of the solvent, the better the resolution of the column (and also the plate count due to the increased mass transport).⁴ Lower viscosity also leads to lower backpressure and, therefore, less stress on the column material. Therefore, for highly viscous solvents a higher operation temperature is strongly recommended to reduce the viscosity of the solvent and to increase the overall performance of the GPC/SEC experiment.

Because of the fact that the swelling of the pores, the polymer dimension and the polymer diffusion are all influenced by the temperature, it is very hard to predict how a temperature change will influence the results. As a rule of thumb, increasing temperatures leads to better resolution and polymer solubility. But there are some exceptions regarding solvent quality and solvent-polymer interactions.

Detectors and Temperature

While for many applications with low solvent viscosity (i.e., systems in THF) temperature control for the columns is not required, detectors based on bulk solution properties (i.e., refractive index or viscosity) must be carefully thermostated to maintain the required baseline stability. Poorly thermostated detectors show less stable baselines and often strong drifts.

This leads to less reproducible molar mass results. Therefore, a reliable thermostation is required for RI detectors and on-line viscometers.

References

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