Field Flow Fractionation: Thermal

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Introduction

Field flow fractionation (FFF) represents a class of separation techniques, which are one-phase methods. They are preferable for the separation and characterization of mixtures such as high molecular weight polymers which might be modified or damaged in two-phase separation methods like chromatography. FFF uses a force field perpendicular to the direction of separation to control the longitudinal velocity of particles injected into the system. It is achieved by the particle redistribution in a flow with a parabolic velocity profile due to the transverse force action. In Thermal FFF (ThFFF), the transverse movement of the particles is caused by the particle 'thermophoresis' in the temperature gradient. The transverse particle velocity, U, is defined by the expression:

$$U = b_T \cdot \nabla T \qquad [1]$$

where b_T is the particle thermophoretic velocity, and ∇T is the transversal gradient of the temperature in the channel. The particle thermophoresis is commonly related to the osmotic pressure gradient produced in the surface layer due to the temperature gradient. This excess osmotic pressure is established in the particle surface layer due to accumulation of the solvent or dissolved molecules or ions in the particle surface layer. This accumulation is related to the particle surface potential Φ. This surface potential may have the electrostatic nature, when the particle surface carries electric charge, or represent some kind of dipole–dipole interaction, when ion adsorption or surface group dissociation is impossible. The latter situation should be characteristic for organic solvents, where dispersion interaction between the particle surface and solvent molecules should play the main role. The theory of thermophoresis is developed mainly for particles larger in size than the characteristic thickness of the surface layer and having moderate surface potential of several kT (k is the Boltzmann constant), which interacts with dissolved ions or molecules. These ions or molecules should be present at a concentration low enough to avoid the excluded volume effects in their accumulation in the particle surface layer. In this situation, the particle thermophoretic mobility may be written as

$$b_T = \frac{3kc_0}{\eta(2+n)}\int_0^\infty y\,\mathrm{d}y\left(1+n\frac{y}{R}\right)\left[\mathrm{e}^{-(\Phi/kT)}\left(\frac{\Phi}{kT}+1\right)-1\right] \qquad [2]$$

where c_0 is the solute concentration in the carrier liquid, η is the carrier liquid viscosity, R is the particle diameter, n is the particle-to-liquid thermal conductivity ratio, and y is the transverse coordinate in the surface layer. The immediate physical factor for the particle thermophoresis is the 'slip' liquid flow in the particle surface layer due to the osmotic pressure gradient, which is related to the temperature gradient in the particle surface layer established along the macroscopic temperature gradient in the liquid. Thus, the main physical events in thermophoresis take place near the particle surface, though the temperature gradient near the particle surface playing the role of the driving force for the particle is defined by the particle and liquid thermal conductivity, which are bulk properties. However, one can expect that these bulk properties will be the same for small particles and larger samples of the material, and the particle thermal conductivity can be obtained from literature data on thermal conductivity of the material or independent experimental determination. It means that particle thermophoresis is mainly related to particle surface properties. It becomes absolutely true for metal particles with very high thermal conductivity, when the parameter n in eqn [1] is very large. For metal particles, the particle thermophoretic mobility is a function of the particle surface properties only. For smaller particles with higher surface potentials, eqn [1] is not true due to intensive solute transport in the particle surface layer.

This surface transport should be compensated by the solute diffusion outside the surface layer, and which, in turn, leads to the solute concentration gradient and related electric field establishment (in electrolytes) around the particle (so-called concentration polarization). However, for a particle with moderate size and thermal conductivity having a surface potential about two to four kT, we can state that the particle thermophoretic mobility is defined by the particle surface properties and does not depend on its size. For emulsion droplets, the thermophoretic mobility in the absence of concentration polarization is determined as:

$$b_T = -\frac{3kc_0R \cdot \nabla T}{(2\eta + 3\eta_\mathrm{i})(2+n)} \int_{-\infty}^{\infty} \left(1 + n\frac{y}{R}\right) \times \left[\mathrm{e}^{-(\varepsilon/kT)} \left(\frac{\phi}{kT} + 1 \right) - 1 \right] y\, \mathrm{d}y \qquad [3]$$

where η_i is the viscosity of the liquid inside the droplet. For homopolymer chains, it is shown by ThFFF experiments, that chain thermophoretic mobility does not depend on chain length and branching, and one can expect that eqn [2] will define it accurately, where R will be the monomer radius. The theory of particle thermophoresis may be true, if some solutes present at low concentration, for example, salt ions, are accumulated around the monomers. However, in true polymer solutions, where no dissolved extrinsic solutes are present, excluded volume effects cannot be neglected, and eqns [2] and [3] cannot be used for the description of thermophoretic behaviour.

For calculation, the Boltzmann exponent indexes in eqns [2] and [3] may be simplified using the approximation:

$$\frac{\Phi}{kT} \approx -\varepsilon\left(1 - \frac{x}{h}\right) \qquad [4]$$

where ε is the depth of the surface potential well in kT units, and h is the characteristic width of this well. Typical orders of values for different kinds of surface potentials are present in **Table 1**, where A is the Hamaker constant, d is the solute radius, q is the solute electric charge, ζ is the particle zeta-potential, and λ is the Debye length.

For the characteristic relaxation time, the Boltzmann transverse particle distribution is established in the system by forcing injected particles toward the wall of the channel and by their diffusion motion. In ThFFF, particles of the same size with higher thermophoretic mobility will be accumulated more closely to the wall, while particles of lower thermophoretic mobility will form a more diffuse layer that extends further into the flow of the carrier liquid. For particles with about the same thermophoretic mobility, the thickness of this layer may also be different, if particles have different diffusion coefficients, D. Particles with higher diffusion coefficient (i.e., with smaller size) will be accumulated in a more extensive layer due to more intensive thermal movement. The thermophoretic mobility related to the surface potential is an important parameter interrelated to the particle surface charge density (where it represents the electrostatic potential) and characterizing the particle surface properties and the possible exchange of substances between the particle and the surrounding liquid. Also, the separation of particles of the same material but with different sizes may be important in the characterization (molecular mass distribution) of commercial latex and polymer particles.

ThFFF is carried out in a thin channel of rectangular cross-section with a width to thickness ratio (aspect ratio) of about 100 (thickness about 10–100 microns). It allows the separation system to approximate to the laminar flow between infinite parallel plates, which is characterized by a parabolic velocity profile, where the fluid velocity at the channel walls is zero, and a maximum in the centre of the channel. Thus, if a group of particles are accumulated, maintaining an average distance from the wall different from another group of particles, their velocities along the channel will be different. As a consequence, they will leave the channel at distinct times, related to the particle thermophoretic mobility and size, which defines the particle diffusion coefficient. There are no other direct methods, where temperature gradients are used for particle, droplet or macromolecule separation. FFF systems are elution methods and allow the collection of fractions during a separation.

Table 1

Surface potential	*Analytical expressions for the Φ(y), ε and h*			*The ranges of values for parameters ε and h*	
	$\Phi(y)$	ε	h	ε	h
Van der Waals forces	$-A(d/r)^6$	A/kT	$d/3$	5–50*	10^{-8} cm (low-molecular surfactant)
Coulomb electrostatic forces	$-q\zeta\,\mathrm{e}^{-(y/\lambda)}$	$q\zeta/kT$	λ	0–10	10^{-7}–10^{-4} cm** (aqueous electrolytes)
Adsorption forces	None	None	None	0–10	$\approx 10^{-7}$ cm
Structure forces	None	None	None	0–10	$\approx 10^{-5}$ cm

*The maximum values of Hamaker constant are reached for metals

**The maximum value of the Debye length is calculated for the deionized water.

Channel Configuration and Construction Limitations

In thermal FFF the temperature gradient across the channel thickness is maintained by the electrical heating of a polished metal block (usually a chrome or nickel-plated copper block) forming one wall and a cooled similar block forming the opposite wall. The plating improves resistance to corrosion, the factor limiting the range of permitted solvents and the separated particles and macromolecules. Cooling is usually accomplished by passing cold water through longitudinal holes bored in the block. To prevent thermogravitational convection, it is the upper block that is heated and the bottom one cooled. Thermocouples are mounted in the blocks to control their temperatures. In the bottom block, capillaries for the introduction and elution of the solvent and the sample are placed. The copper blocks are separated by a spacer of a polymer material with a low thermal conductivity (Mylar, Kevlar, etc.) to provide high temperature gradients. The channel constructions are described more exactly in the literature (see Further Reading). One of the main advantages of the FFF family stems from the uniform open channel geometry and the well-defined flow profile. As a consequence, retention can be related directly to the physicochemical parameters of the analyte material and carrier liquid. Possible deviations of the flow profile and the polymer parameters due to the non-uniform temperature distribution have been described.

Polymer Characterization

Progress in ThFFF instrumentation and methodology has allowed a systematic study on the thermal diffusion of polymer solutions. The success of these studies is provided by the ability of ThFFF to produce accurate values of thermal diffusion parameters using small quantities of polymer (a few hundred micrograms). The values of the thermal diffusion coefficients (parameters equal to the thermophoretic mobility) have been obtained for 17 polymer–solvent systems and are about 10^{-8}–10^{-7} $\mathrm{cm^2/s \cdot K}$, and their molecular masses are from about several tens to about hundred Daltons. The results show the correlation of the polymer thermophoretic mobility with several polymer and solvent parameters, the thermal conductivity of the polymer and solvent, the polymer density, and the viscosity and viscous activation energy of the carrier liquid. Studies also demonstrated a correlation of the polymer thermophoresis parameters with the solvatation properties of the solvent. Though conventional diffusion in polymer solutions is well defined, the thermal diffusion of polymers in liquids is not exactly understood and not well characterized. Although there are equations relating retention to experimental parameters and transport coefficients of polymers, values of polymer thermophoretic mobility are not commonly available, and a model for predicting them from physicochemical parameters is in progress only. Therefore, a calibration is necessary for characterizing the molecular weight distribution (MWD) of polymers by ThFFF (although a single calibration point can be used, when the dependence of the diffusion coefficient on molecular weight is known). Calibration is simple in the analysis of homopolymers because well-characterized molecular weight standards are available for a variety of polymers.

The characterization of copolymers presents more problems because of the overlapping effects of composition and molecular weight distribution (MWD). Often it is necessary to characterize both the MWD and the compositional distribution. In this case the commonly used method of size exclusion chromatography (SEC) is not adequate because the separation is governed by size alone. Thus, molecular weight fractions with different compositions may be eluted in SEC simultaneously. In contrast, ThFFF may separate polymers by both chemical composition and size, and is therefore capable of yielding both size and compositional information on copolymers. Separation by size in ThFFF is governed by differences in the diffusion coefficient of the polymers, while separation by chemical composition may result from differences in the thermophoretic mobility.

The results on ThFFF of random and block copolymers of polystyrene (PS) and polyisoprene (PI) in tetrahydrofuran and cyclohexane show that for random copolymers and block copolymers with a random configuration in solution, the thermophoretic mobility is a linear function of monomer composition. It may be a basis for obtaining compositional information on such copolymers by ThFFF. For copolymers with a radial segregation of monomers, thermophoresis is determined mainly by monomers located in the outer region of the polymer coil. The dependence of retention on the radial distribution of monomers provides a basis for evaluating bonding arrangements in copolymers. The further progress in copolymer characterization by ThFFF is related to progress in the theory of the polymer thermophoresis.

Particle Characterization

Though most ThFFF samples are polymers, the ability of ThFFF to retain and separate both submicron and micron size particles (latex and silica) suspended in various organic carrier liquids has also been demonstrated by Shiundu, Lee and Giddings. In their article, the dependence of particle retention on various factors (solvent properties, amount of added electrolyte, particle size and composition, and cold-wall temperature) is evaluated and discussed.

Thermophoretic mobilities of several latex-solvent combinations have been obtained from the ThFFF retention data. The studies were carried out in polar organic solvents, cyclohexane and aqueous carriers. As a rule, the thermophoretic mobilities of particles range from 10^{-8} to 10^{-7} $\mathrm{cm}^2/\mathrm{s}\cdot\mathrm{K}$, while the particle size ranges from about 0.04 to about 1 micron.

The retention of colloidal particles in ThFFF demonstrates a strong dependence on the chemical composition of the particles or their surfaces. These results are observed among both similar particles (such as latex particles) and different particles (including latex particles, and inorganic and metallic colloids). These compositional effects are observed for particles suspended in both aqueous and non-aqueous carrier liquids. Also, metal particles (e.g. palladium) are less retained than silica particles, with latex particles most retained. The resolution of particles of equal size in ThFFF experiments is also demonstrated. Surface compositional effects were also demonstrated in this study. These effects confirm the possibility of colloid particle surface analysis by thermal FFF.

Combined Electric-Thermal FFF (El-ThFFF)

An interesting combined technique represents the application of an electric field across the channel for Thermal FFF, where a temperature gradient is also established. For details see Particle Size Separation / Field Flow Fractionation: Electric Fields.

Conclusion

ThFFF is a method for the particle and macromolecule separation in electrolyte and non-electrolyte solvents according to their interaction with the solvent molecules or/and ions of the added salt. For particles, these are surface interactions, though the particle/solvent thermal conductivity ratio is also important. Thermophoretic mobility may be calculated immediately from ThFFF experimental data, when the particle or macromolecule diffusion coefficient is known. This parameter may depend on both electrostatic and non-electrostatic (dispersion) interactions and can be used for their characterization. Also, the thermophoretic mobility may be used for the characterization of surface particle and macromolecule properties, when the respective theory is developed.

See also: **II / Particle Size Separation:** Field Flow Fractionation: Electric Fields; Theory and Instrumentation of Field Flow Fractionation. **III / Colloids: Field Flow Fractionation. Polymers:** Field Flow Fractionation.

Further Reading

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