

Mechanism of Polymer Thermophoresis in Nonaqueous Solvents

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The thermophoresis of homopolymer chains dissolved in a pure nonelectrolyte solvent is theoretically examined. Using a similar approach to that used for suspended particles, thermophoresis is related to the temperature-dependent osmotic pressure gradient in the solvent layer surrounding the monomer units (mers). The gradient is produced by small changes in the concentration of solvent molecules (i.e., solvent density) as a result of the mer–solvent interaction energy. The resulting expression contains the interaction energy as well as solvent thermodynamic parameters, including the cubic coefficient of thermal expansion, the isothermal compressibility and its temperature coefficient. Using the general dependence of dipole–dipole potentials on the distance between interacting objects, an expression for thermophoretic mobility that contains a characteristic Hamaker constant is obtained. The resulting expression is used to calculate interaction constants for polystyrene and poly(methyl methacrylate) in several organic solvents using thermophoresis data obtained from thermal field-flow fractionation. The calculated constants are compared to values in the literature and found to follow the same order among the different solvents. Furthermore, the model is consistent with laboratory measurements of polymer thermophoresis, which is weak in water compared to less polar solvents, and which correlates with monomer size. In nonelectrolyte solvents, London dispersion forces must play a major role since other dipole–dipole interactions are insufficient to produce the required interaction energies. Finally, the model predicts that to have a measurable thermophoretic mobility in a given solvent, the polymer should have a Hamaker constant that is greater than 10–15 kT , as calculated by simple but commonly used theoretical models.

Background

The experimental study of polymer thermophoresis was renewed during the past decade in conjunction with the development of thermal field-flow fractionation (ThFFF), a high-resolution technique that uses thermophoresis to separate and characterize polymers on an analytical scale.¹ Because ThFFF utilizes a thin open cell, the dependence of polymer retention on parameters that are used to quantify thermophoresis is well defined. As a result, ThFFF is capable of measuring such parameters with high precision.² In a ThFFF study of polystyrene,³ for example, the independence of polymer thermophoresis on chain length and branching was demonstrated. In a separate ThFFF study, the thermophoretic properties of polystyrene, poly(α -methyl)styrene, poly(methyl methacrylate) and polyisoprene in several organic solvents⁴ were used to examine a variety of theories of polymer thermophoresis proposed by different authors. Unfortunately, the theories failed to predict major trends in the measured values of thermophoresis with polymer or solvent properties. However, the work clearly demonstrated that polymer–solvent interactions play an important role in polymer thermophoresis.

The independence of polymer thermophoresis on chain length and branching was predicted by physical arguments that long-range interactions between monomer units (mers) are not

important in thermophoresis,⁵ and therefore a homopolymer chain could move in thermophoresis with the same velocity as each mer separately. As a result, we can model polymer thermophoresis using the same approach as that used in particle thermophoresis, considering the mers as spherical particles for the sake of simplicity. This approach considers the flow of liquid caused by the gradient of osmotic pressure in the surface layer of the particle.⁶ At this stage, the interactions between mers are ignored.

In the case of suspended particles, the excess osmotic pressure $p - p_0$ in the surface layer due to the solute accumulation is written as

$$p(y) - p_0 = kTc_0[e^{-\Phi(y)/kT} - 1] \quad (1)$$

where k is Boltzmann's constant, T is the temperature, c_0 is the solute concentration in a liquid, $\Phi(y)$ is the surface potential responsible for solute accumulation, p_0 is the macroscopic pressure in the bulk liquid, and r is the coordinate normal to the particle surface. Equation 1 assumes that the solute concentration in the surface layer is low enough that the volume occupied by the accumulated solutes may be neglected. This assumption may hold for suspensions in which the solute concentration does not exceed 10^{-3} – 10^{-2} M. However, in polymer solutions with no added solutes, only the solvent molecules can take part in the accumulation process. The free volume in liquids, which is the only volume available for solvent

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TABLE 1: Properties of Solvents Examined in Ref 3; Data Taken from Ref 9

solvent	electrical conductivity (ohm ⁻¹ cm ⁻¹)	dielectric const	dipole moment × 10 ¹⁸ (esu cm)	thermal conductivity (cal s ⁻¹ cm ⁻¹ K ⁻¹)
Nonpolar Solvents				
cyclohexane	7 × 10 ⁻¹⁸	2.02		
benzene	4.43 × 10 ⁻¹⁷	2.27	0	
toluene	8.0 × 10 ⁻¹⁶	2.38	0.31	0.0003083
ethylbenzene	0	2.4	0.37	
Polar Solvents				
2-butanone	3.6 × 10 ⁻⁹	18.51	2.76	0.000358
tetrahydrofuran	4.5 × 10 ⁻⁵ –9.3 × 10 ⁻⁸	7.58	1.75	0.000336
ethyl acetate	<10 ⁻⁹	6.05	1.82	

accumulation, i.e., increased density, is 10–20% of the entire volume occupied by the body of the molecules,⁷ as indicated by the volume change associated with melting. Because of this limitation in free volume, the Boltzmann distribution associated with eq 1 is inappropriate. Nevertheless, variations in solvent concentration, which lead to an osmotic pressure gradient in the mer surface region, should be considered and analyzed as a driving force in polymer thermophoresis.

In the most papers on the particle electro-, diffusio-, and thermophoresis, the thickness of the surface layer is assumed to be much smaller than the radius of the particle. An exception is outlined in ref 8, where particle electrophoresis is examined with an arbitrary surface layer thickness. Although the approximation of a thin surface layer may be true for suspended colloids with a radius 0.1 μm or more, it does not hold for mers, which have a size that exceeds that of the solvent molecules by several times at most. In this work, the model developed in ref 8 is modified for thermophoresis, to evaluate the hydrodynamic situation involved with the movement of solvent molecules in the vicinity of mers.

Most ThFFF experiments on polymers have been carried out in organic solvents with low electric conductivity, so that ions are absent and polymer dissociation does not occur to a significant extent. The properties of the solvents used in ref 3 are summarized in Table 1. In such solvents, where the ions are present in vanishing quantities, only dipole–dipole interactions play a role.¹⁰ Dipole–dipole interactions include those between permanent dipoles (the Keesom interaction), those between permanent and induced dipoles (the Debye induction interaction), and those that are induced spontaneously (the London or dispersion interaction). According to the Fowkes approach,¹⁰ these dipole–dipole interactions have a common dependence on the distance between dipoles and may be written in the following simple form:

$$\Phi(r) = -\frac{16A(r_m r_0)^3}{9r^6} \quad (2)$$

Here A is the Hamaker constant used in colloid chemistry, which characterizes the potential energy of dipole–dipole interactions between mers of radius r_m and solvent molecules of radius r_0 . The closest approach distance (r_{\min}) between interacting molecules in the Fowkes model is approximated by $r_{\min} = \sqrt{r_m r_0}$. This approximation compensates for a discrepancy that occurs at short distances when eq 2 is used in place of the exact form of the interaction potential. In most situations where the model is applied, $r_m \approx r_0$ (the relative difference is <10%); therefore, $r_{\min} \approx r_m$. The significance of these approximations in the use of eq 2 to define the monomer–solvent interaction potential is discussed below.

The interaction constant A depends on the permanent dipole moments of the monomer and solvent molecules and on the

low and high-frequency electric susceptibilities, which govern London dispersion forces.¹⁰ For calculating thermophoretic mobilities, only the coordinate dependence of the interaction potential ($\Phi(r) \sim r^{-6}$) is important. The derived expressions will be compared with experimental data, and where possible, values of the Hamaker constant A will be extracted for specific mer–solvent pairs. Furthermore, these values will be used to form certain conclusions as to the kind of dipole–dipole interactions responsible for polymer thermophoresis. Data on intermolecular interactions collected in refs 10 and 11 indicate that dispersion forces are the primary type of dipole–dipole interactions between mer and solvent in nonpolar to moderately polar liquids.

The derivation of thermophoretic mobility can be divided into three stages: (1) calculation of the temperature distribution around the mer, (2) derivation of the solvent molecule concentration and related osmotic pressure distribution around the mer due to monomer–solvent interaction, and (3) derivation of the general expressions for the solvent velocity profile around the mers, the mer thermophoretic velocity, and the polymer thermophoretic mobility using eq 2 for the mer–solvent interaction potential.

Results

Temperature Distribution around the Mer. The first stage of the temperature distribution calculation is carried out in many papers on particle thermophoresis (see for example, refs 6 and 9). We discuss the formulation of the problem and the final results only, considering the mer to be a spherical particle.

It is assumed that the temperature distributions inside and outside the particle (T_i and T_e , respectively), as obtained from the temperature conduction equation, have the following dipole form:

$$T_i = \nabla T r \cos \vartheta \quad (3)$$

$$T_e = T_0 + \nabla_i T r \cos \vartheta + \frac{M_T}{r^2} \cos \vartheta \quad (4)$$

where T_0 is the temperature at the center of the particle, r is the distance from its center, ϑ is the angle between the radius vector \vec{r} and the outer temperature gradient ∇T , M_T is the temperature “dipole moment” of the particle, and $\nabla_i T$ is the internal temperature gradient in the particle. On the mer surface, at $r = r_m$, we have the following boundary conditions:

$$T_i = T_e \quad (5)$$

$$\theta_i \frac{\partial T_i}{\partial r} = \theta_e \frac{\partial T_e}{\partial r} \quad (6)$$

where θ_i and θ_e are the thermal conductivities of the particle and external liquid, respectively. Equations 3–6 give the

complete picture of the temperature distribution around the monomer particle. Using the definition $M_T = \nabla T(n-1)/(n+2)r_m^3$, eq 4 can be expressed in following alternative form:

$$T_e = T_0 + \nabla T r_m \cos \vartheta \left(\frac{r}{r_m} + \frac{n-1}{n+2} \frac{r_m^2}{r^2} \right) \quad (7)$$

where n is the ratio of mer to solvent thermal conductivity ($n = \theta_i/\theta_e$). For further calculations, it is convenient to write the temperature gradient in vector form:

$$T_e = \vec{\nabla} T \left[1 + \frac{n-1}{n+2} \frac{r_m^3}{r^3} \right] - 3(\vec{\nabla} T \cdot \vec{n}_0) \cdot \vec{n}_0 \frac{n-1}{n+2} \frac{r_m^3}{r^3} \quad (8)$$

where \vec{n}_0 is the unit vector directed along the radius vector \vec{r} .

Solvent Molecule Concentration and Osmotic Pressure Distribution around the Mer. The solvent molecule concentration in a force field obeys the convection-diffusion equation, which takes the following form for concentrated systems¹¹

$$\frac{\partial \phi}{\partial t} = \nabla \left\{ \frac{1}{6\pi\eta r_0} \left[\frac{d\Pi}{d\phi} \nabla \phi + \frac{6\phi}{\pi r_0^3} \nabla \Phi \right] \right\} \quad (9)$$

Here t is the time, η is the dynamic solvent viscosity, Π is the excess osmotic pressure raised around the monomer, Φ is the monomer force potential given by eq 2, and ϕ is the volume fraction of the solvent molecules, which is related to the numeric concentration of the solvent molecules c_0 by

$$\phi = \frac{\pi r_0^3 c_0}{6} \quad (10)$$

when molecules are considered as the hard spheres.¹¹ Under steady-state conditions, the following equation defines the distribution of solvent molecules around the mer:

$$\frac{d\Pi}{d\phi} \nabla \phi + \frac{6\phi}{\pi r_0^3} \nabla \Phi = 0 \quad (11)$$

Equation 11 represents the condition of local hydrostatic equilibrium across the mer surface layer in the direction perpendicular to the surface, as related to the force-field potential.

To define the osmotic pressure resulting from small differences in the local concentration of solvent molecules, we invoke the principles of perturbation theory, which requires a small parameter in order to cancel high-order terms. The value of parameter ϕ (0.8–0.9) is too large in this case: therefore we introduce the small parameter $\delta = 1 - \phi$. By assuming the changes in δ due to the presence of the polymer are small, one can define the osmotic pressure as

$$\Pi = p - p_0 = c_m kT \left[-|p_0'|(\delta - \delta_0) + \frac{p_0''}{2}(\delta - \delta_0)^2 \right] \quad (12a)$$

where p is the local pressure and the subscript in p_0 and δ_0 represent the respective values far from the mer surface, where the interaction potential is zero. Parameter c_m is the densest possible packing concentration ($c_m = 6/\pi r_0^3$ for the hard sphere model) for the solvent molecules, and

$$p_0' = \frac{1}{c_m kT} \frac{\partial p}{\partial \delta} \Big|_{\delta=\delta_0} \quad (12b)$$

$$p_0'' = \frac{1}{c_m kT} \frac{\partial^2 p}{\partial \delta^2} \Big|_{\delta=\delta_0} \quad (12c)$$

Equation 12 is a general expression that relates the osmotic pressure to variations in the solvent molecule concentration, without connecting it to a concrete model equation of state. Such a connection may be necessary to further relate the osmotic pressure to changes expressed by solvent parameters that are related to the state of the pure solvent, and which can be measured independently, as outlined below.

The sign of parameter p_0 in eq 12 should be negative, since pressure is expected to decrease as δ increases. Substituting eq 12 into eq 11 and keeping only the first power of parameter $\delta = \delta_0$ in solving the resulting differential equation, we obtain

$$\int_{\delta_0}^{\delta} \left[-\frac{|p_0'|}{1-\delta_0} + \frac{p_0''(1-\delta_0) - |p_0'|}{(1-\delta_0)^2} (x - \delta_0) \right] dx = -\frac{|p_0'|}{1-\delta_0} (\delta - \delta_0) + \frac{p_0''(1-\delta_0) - |p_0'|}{2(1-\delta_0)^2} (\delta - \delta_0)^2 = -\frac{\Phi(r)}{kT} \quad (13)$$

Solving this quadratic equation, exposing the solution in a power series of the small parameter $\delta - \delta_0$ and keeping only its first and second powers, we have

$$\delta(r, \vartheta) - \delta_0 = \frac{1 - \delta_0}{|p_0'|} \frac{\Phi(r)}{kT(r, \vartheta)} + \frac{1 - \delta_0}{2|p_0'|^3} [p_0''(1 - \delta_0) - |p_0'|] \left[\frac{\Phi(r)}{kT(r, \vartheta)} \right]^2 \quad (14)$$

where the temperature distribution is defined by eq 7.

Substituting eq 14 into eq 12 and keeping only first two powers of the small parameter yields

$$\Pi = c_m \phi_0 \left[-\Phi(r) + \frac{1}{2|p_0'|} \frac{\Phi^2(r)}{kT(r, \vartheta)} \right] \quad (15)$$

Equation 15 defines the excess osmotic pressure in the solvent due to the presence of mers. This expression can be simplified. First, we introduce the cubic thermal expansion coefficient of the solvent (α_T), which is defined as

$$\alpha_T = \frac{\partial \ln v_0}{\partial T} \quad (16)$$

where v_0 is mean volume of the solvent occupied by one solvent molecule:

$$v_0 = \frac{1}{c_m \phi_0} \quad (17)$$

This parameter is related to molar volume (V_0) by $v_0 = V_0/N_A$, where N_A is the Avogadro number. Next, we define parameter $|p_0'|$ in terms of v_0 and the isothermal compressibility of the solvent (β_T):

$$|p_0'| = \frac{v_0}{kT\beta_T} \quad (18)$$

where

$$\beta_T = \left. \frac{\partial \ln \nu_0}{\partial p} \right|_{T=\text{const}} \quad (19)$$

Equations 15–19 can be combined to obtain

$$\Pi = -\frac{\Phi}{\nu_0} + \frac{\beta_T \Phi^2}{2\nu_0^2} \quad (20)$$

$$\nabla \Pi = \frac{\alpha_T}{\nu_0} \left[\Phi + \left(\frac{\partial \beta_T / \partial T}{2\alpha_T} - \beta_T \right) \frac{\Phi^2}{\nu_0} \right] \nabla T \quad (21)$$

In principle, the temperature dependence of any parameter contained in eq 20 could lead to the establishment of an osmotic pressure gradient around the mers. However, terms associated with the temperature dependence of the interaction potential are compensated by the respective volume force arising in the solvent due to spatial changes of the interaction potential. Therefore, only the temperature dependence of solvent parameters c_m , δ_0 , and $|p_0'|$ is considered in eq 21.

Equation 21 represents the expression for the temperature-related osmotic pressure gradient, which will be used to solve the hydrodynamic problem of solvent flow around the mers. This expression is not related to any model equation of state for the solvent and contains only those solvent parameters that can be obtained independently. Solvent parameters that are not readily available can be calculated using a model equation of state for the solvent. In the Discussion, we will consider the validity of the assumptions used in deriving eqs 20 and 21 and conclude that these assumptions are valid within the typical range of solvent parameters encountered.

Flow Velocity Profile around the Monomer Particle and Its Thermophoretic Mobility. The theory of thermophoresis in liquids as surface driven phenomenon is considered in ref 12, where the possibility to express the parameters characterizing the particle thermophoresis through the surface tension was examined. For an excellent review on the diffusiophoresis, where certain common features of diffusi- and thermophoresis are discussed, see ref 13, where much earlier Derjagin ideas on the nature of the thermoosmosis are also mentioned. All the previous theoretical approaches to the theory of the particle diffusi- and thermophoresis were based on the assumption on the linear dependence of the osmotic pressure in the particle surface region on the concentration of solutes accumulated there under the action of a surface potential. The latter concentration was assumed to be Boltzmannian distribution. This assumption cannot be used in this paper, since the concentrations of the solvent molecules around the mers are high, while the macromolecule thermophoresis still could be considered as the phenomenon driven by a gradient of the pressure around the mer.

The flow velocity profile in the mer surface layer is defined by the Navier–Stokes equation

$$\eta \Delta \vec{u} = \vec{f} - \nabla \Pi - \nabla p \quad (22)$$

where \vec{u} is its velocity, \vec{f} is the volume force acting on a unit volume of the solvent, and p is the hydrodynamic pressure raised in the movement of mers. As stated above, the volume force is compensated by the temperature dependence of the interaction potential; therefore these two factors (the latter of which is a component of $\nabla \Pi$) are eliminated from further consideration. In solving eq 22 for a spherical particle, we use the approach taken in ref 8, which utilizes the generalized reciprocal theorem on the invariance of the following integral:

$$\eta \int_S \vec{u}' \cdot \hat{\sigma} \, d\vec{S} + \eta \int_V \vec{u}' \cdot \vec{f} \, dV = \eta' \int_S \vec{u}' \cdot \hat{\sigma} \, d\vec{S} + \eta' \int_V \vec{u}' \cdot \vec{f}' \, dV \quad (23)$$

Here, S is the outer surface of a moving body, V is the outer volume surrounding this surface, and $\hat{\sigma}$ is the hydrodynamic stress tensor expressed by the components of the flow velocity gradient.¹⁴ The primed and unprimed parameters in eq 23 are interrelated in two separate problems on the movement of the same body. The theorem was proven in ref 8 for the case when only a volume force is acting in a liquid and the osmotic pressure gradient is absent. However, the structure of the Navier–Stokes equation (eq 22) allows the external volume force in a liquid to be interchanged with a predetermined “external” pressure gradient. Thus, the reciprocal theorem can be “generalized” to situations where only the predetermined pressure gradient, related to the osmotic pressure, is present in a liquid. Using this generalization, we employ the results of ref 8 which relates particle phoresis to the volume force and fluid velocity distribution in the space around a particle moving with constant unit velocity $\vec{U}_1(\vec{r})$. Here, \vec{r} is the radius vector directed from the particle center to the observation point, analogous to the temperature distribution problem. The velocity distribution, which corresponds to the conditions, is defined as¹⁴

$$\vec{U}_1(\vec{r}) = \frac{3}{4} \frac{r_m}{r} [\vec{u}_0 + \vec{n}_0 \cdot (\vec{u}_0 \cdot \vec{n}_0)] + \frac{1}{4} \left(\frac{r_m}{r} \right)^3 [\vec{u}_0 - 3\vec{n}_0 \cdot (\vec{u}_0 \cdot \vec{n}_0)] \quad (24)$$

where \vec{u}_0 is the unit vector directed along the \vec{U}_1 vector, and \vec{n}_0 is the unit vector directed along the radius vector. Instead of the volume force considered in ref 8, we combine the osmotic pressure gradient defined in eq 21 with the temperature gradient distribution defined in eq 12. Using the steady-state condition that the sum of the hydrodynamic friction force and the thermophoretic force acting on the monomer is equal to zero, we obtain the following general expression for the thermophoretic velocity U_T :

$$U_T = \frac{1}{6\pi\eta r_m} \int_0^\pi \sin \vartheta \, d\vartheta \int_{r_m}^\infty 2\pi r \, dr \frac{d\Pi}{dT} (\vec{U} \cdot \vec{\nabla} T) \quad (25)$$

Next, we need to substitute expressions for the temperature gradient and temperature derivative of the osmotic pressure into eq 25.

By substituting eqs 2, 8, 21, and 24 into eq 25 and carrying out some simple but cumbersome integral calculations, we obtain the following expression for the thermophoretic velocity of the mer, and therefore of the entire homopolymer chain:

$$U_T = \frac{\alpha_T r_m^2}{3\eta} \left[- \left(1 + \frac{1}{28} \frac{n-1}{n+2} \right) \frac{A}{9\nu_0} + \frac{2\beta_T}{5} \left(1 + \frac{5}{364} \frac{n-1}{n+2} \right) \left(\frac{\partial \ln \beta_T}{\partial T} - 1 \right) \left(\frac{16A}{9\nu_0} \right)^2 \right] \nabla T \quad (26)$$

The parameter $n - 1/n + 2$ changes from $-1/2$ at $n = 0$ to 1 as $n \rightarrow \infty$; therefore the two terms in eq 26 that contain this parameter are negligible. Thus, the difference in thermal conductivities of the mer and solvent is not a significant factor in polymer thermophoresis. This important result is discussed further in the Discussion.

Ignoring the negligible terms, the thermophoretic mobility b_T , which is defined as the thermophoretic velocity per unit

temperature gradient, is expressed as

$$b_T = \frac{\alpha_T r_m^2}{3\eta} \left[-\frac{16A}{9\nu_0} + \frac{2\beta_T}{5} \left(\frac{\partial \ln \beta_T}{\partial T} - 1 \right) \left(\frac{16A}{9\nu_0} \right)^2 \right] \quad (27)$$

Equation 27 contains two parameters that characterize the mer, namely its radius (r_m), and its interaction potential with the solvent (A). The equation also contains several parameters that characterize the solvent: the cubic thermal expansion coefficient (α_T), the isothermal compressibility (β_T) and its temperature coefficient ($\partial \ln \beta_T / \partial T$), and the solvent viscosity (η). The parameters characterizing the solvent may be measured independently, and many are tabulated (see, for example, ref 9). The measurement or calculation of monomer hydrodynamic radius is discussed in the Discussion. Only the temperature coefficient of the solvent compressibility may present a problem in its determination, but it is only a major factor when the Hamaker constant is very high. For a preliminary evaluation of the model using experimental data, we ignore the compressibility term in using the following simplified form of eq 27:

$$b_T = -\frac{16\alpha_T r_m^2}{27\eta} \frac{A}{\nu_0} \quad (28)$$

Discussion

Before discussing the properties of polymer thermophoresis that follow from eq 27, we examine the validity of the assumptions accepted in the calculations. The main assumption is that changes in the solvent state due to solvent–mer interactions are small. According to the Carnahan–Starling model, which is applicable to hard spheres, the following equation of state defines the dependence of excess osmotic pressure on concentration:⁷

$$p = \frac{6kT}{\pi r_0^3} \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3} \quad (29)$$

In the case considered here, where $\delta \ll 1$, eq 29 can be written as

$$p_0 \approx \frac{2kT}{\nu_0 \delta^3} \quad (30)$$

Substituting eq 30 into eq 14, we obtain

$$\delta - \delta_0 = \frac{\delta_0^4}{6} \frac{\Phi(r)}{kT} + \frac{\delta_0^7}{18} \left[\frac{\Phi(r)}{kT} \right]^2 \quad (31)$$

Recalling that parameter δ_0 has characteristic values in the range 0.1–0.2, while parameter A in eq 2 ranges from 1 to 100 kT ,⁴ one can see that changes in solvent concentration due to mer–solvent interactions are in fact very small.

Changes in solvent pressure due to the presence of polymer can be evaluated using eq 20 and solvent parameters summarized in Table 2. Typical values of parameter α_T are 10^{-3} K^{-1} , while those of parameter β_T are $10^{-10} \text{ cm}^2 \cdot \text{dyne}^{-1}$. Typical values of parameter ν_0 are $2 \times 10^{-22} \text{ cm}^3$, as calculated by $\nu_0 = M/dN_A$, where M is the molar mass of the solvent and d is its density. Using eq 31 for the pressure in pure solvent, and the typical

TABLE 2: Solvent Parameters Used To Evaluate Eq 20; Data Taken from Ref 9

solvent	$\alpha_T (\text{K}^{-1})$	$\eta (\text{cP})$	$M (\text{g})$	$d (\text{g} \cdot \text{cm}^{-3})$
cyclohexane	0.0012	0.98	84	0.78
benzene	0.0012	0.65	78	0.89
toluene	0.0011	0.55	92	0.87
ethylbenzene		0.64	106	0.87
methylethyl ketone	0.0012	0.40	72	0.80
tetrahydrofuran	0.0011	0.46	72	0.89
ethyl acetate	0.0014	0.40	88	0.90

values of α_T , β_T , ν_0 , eq 20 describing the pressure change due to mer–solvent interactions may be written in the following form:

$$p \approx \frac{kT}{\nu_0} \left[2 \times 10^3 - \frac{\Phi}{kT} + 10^{-2} \left(\frac{\Phi}{kT} \right)^2 \right] \quad (32)$$

where the values $kT = 4 \times 10^{-14} \text{ erg}$ and $\delta = 0.1$ are used. From eq 32 it can be shown that the contribution of mer–solvent interactions is small enough that it does not exceed 10% even at $\Phi \approx 10^2 kT$, which represents the uppermost limit for the dipole–dipole interaction value.⁷ This evaluation also shows that the quadratic term in eq 27 is small in comparison to the linear term, so that the expression for homopolymer thermophoretic mobility can be written as

$$b_T = -\frac{16\alpha_T r_m^2}{27\eta} \frac{A}{\nu_0} \quad (33)$$

In eq 33, the terms describing the temperature distribution around the mers due to differences in the thermal conductivities of the mer and solvent are absent. Compared to particle thermophoresis,⁶ the thermal conductivity difference is not significant with dissolved polymers because the layer where the pressure gradient is raised is not thin in comparison to the monomer size. Only in the thin layer around the particle is the temperature distribution arising from a particle–solvent thermal conductivity difference important. Far from this layer, at a distance of about one particle radius, the temperature differences vanish. In polymer solutions, where the osmotic pressure gradient is established within a distance of about one mer radius, thermophoresis is defined mainly by the macroscopic value of the temperature gradient located at the center of the mer.

In eq 33, values for parameters r_m and A still require determination. Measurements of polymer thermophoresis by ThFFF can be used for the determination of one of these remaining parameters if the other one is measured or calculated independently. Parameter r_m can be obtained from experiments that measure those hydrodynamic properties of the macromolecule that are connected in a simple way to monomer dimensions. For example, an independent measure of r_m can be obtained from the dependence of the polymer chain self-diffusion coefficient on polymer length in dilute solutions under Θ conditions. Also, intrinsic viscosity measurements under Θ conditions may be used to obtain r_m values if the dependence of viscosity on molecular weight is obtained.¹⁵ These methods relate the friction coefficient of the mer in the appropriate solvent to the hydrodynamic radius by the Stokes–Einstein equation. However, such methods are valid only for very persistent polymers, where the Gaussian segment length coincides with the mer hydrodynamic radius. An approximation of the mer hydrodynamic radius can also be made using the hard sphere model, where the volume occupied by one mer in a crystal

TABLE 3: Estimation of Monomer and Solvent Radii

solvent	
cyclohexane	$r_0 = 6.99 \text{ \AA}$
benzene	$r_0 = 6.52 \text{ \AA}$
toluene	$r_0 = 6.95 \text{ \AA}$
ethyl benzene	$r_0 = 7.29 \text{ \AA}$
methyl ethyl ketone	$r_0 = 6.59 \text{ \AA}$
tetrahydrofuran	$r_0 = 6.36 \text{ \AA}$
ethyl acetate	$r_0 = 6.77 \text{ \AA}$
monomer	
styrene	$r_m = 7.16 \text{ \AA}$
methyl methacrylate	$r_m = 6.99 \text{ \AA}$

consisting of mer spheres may be written as

$$\nu_m = \frac{\pi r_m^3}{6} = \frac{M_m}{d_m N_a} \quad (34)$$

Here, M_m and d_m are the molecular mass and density of the mer, respectively. When the density d_m is not known, it can be approximated by the density of the liquid monomer. The relative error in such a substitution will be about δ^{-3} , or several percent to 10%. Furthermore, one obtains the equivalent geometric radius of the monomer instead of its hydrodynamic radius. The mer and solvent molecule radii calculated in this way are summarized in Table 3. Only monomers that exist as liquids are present in Table 3, to restrict our evaluation to data obtained from a single source.⁹ The values of r_m in Table 3 are similar to the hydrodynamic radii reported in ref 15.

Using eq 33 and the data summarized in Tables 2 and 3, the Hamaker constant A was calculated from measured values³ of the polymer thermophoretic velocity. The resulting values are summarized in Table 4. It is interesting to compare the values of A in Table 4 with values obtained using other methods. There is no direct data on mer–solvent interaction parameters; therefore we will use the following equation to calculate mer–solvent interaction constants from monomer–monomer and solvent–solvent interaction parameters found in the literature:^{16,17}

$$A = \sqrt{A_{m-m} A_{s-s}} \quad (35)$$

Here A_{m-m} and A_{s-s} are the monomer–monomer and solvent–solvent Hamaker constants, respectively. Equation 35 is based on a simple model of molecule–molecule interactions in the liquid state.^{16,17} The most complete table of the solvent–solvent interaction constants was found in ref 18, while styrene–styrene interaction constants were found in ref 19. The interaction constants calculated in this way are summarized in Table 5.

The absence of a range in the values reported in Table 5 does not mean that different approaches to calculating interaction constants yield the same value, but rather the lack of references in which a wide range of data was obtained. For example, the value of A_{m-m} for cyclohexane in parentheses was calculated using the ionization potentials, and differs significantly from the value obtained by the alternative approach of re 18. Likewise, A_{m-m} for styrene is reported as a range of possible values in ref 19. As an earlier work demonstrated,²⁰ by choosing the most convenient values within a wide range of reported A_{m-m} values, polymer thermophoresis can be shown to correlate strongly with such values. However, such a correlation has little significance unless all the values were calculated from the same method. Therefore, for the purpose of evaluating the model proposed in this work, we utilize A_{m-m} values obtained from a common source.

Table 6 compares the mer–solvent interaction constants for polystyrene, calculated from eq 33 using thermophoretic mobili-

ties from the literature, with the values calculated from eq 35 using data on A_{m-m} and A_{s-s} from the literature.^{17–19} The values agree within an order of magnitude. However, the values calculated from eq 33 are consistently lower. The analogous calculations with methyl methacrylate lead to the same result. The discrepancy between values obtained by the two methods is not unexpected considering the simplifications used in the calculations. For example, systematic errors can be expected to result from the assumption of hard spheres in the calculations of r_0 . Since the aim of this paper is to examine the polymer thermophoresis mechanism rather than develop a new method for calculating interaction constants, the discrepancy may be considered acceptable. More important is the fact that the order of the value for A_{m-s} in the different solvents is the same for the two methods. This consistency supports the validity of the thermophoretic model.

Another simplification of the thermophoretic model, which could lead to the discrepancy between interaction constants calculated using the two methods discussed above, is associated with neglecting the interaction between mers. Although the coupling of heat and mass flux is mainly localized around each mer, the interaction between mer and solvent will be affected by other mers. Such secondary affects are neglected in the current model, but are essential components to refining the model, and will be the focus of a future publication.

An important conclusion of this analysis is that thermophoresis is highly sensitive to the size of the mer. It is important, therefore, to have accurate values of the mer radius if the model is to be used to either measure interaction constants or estimate polymer thermophoresis. The latter is important in the application of ThFFF to new and different polymers. On the other hand, the model demonstrates that in order for a solvent to be successfully used to separate polymer by ThFFF, interaction constants calculated using contemporary methods¹⁶ must have a magnitude on the order of 10–15 kT . These conclusions may be used in the search of new solvents for polymer ThFFF, and as tool for further evaluating the model of polymer thermophoresis proposed in this study.

The general agreement between interaction constants calculated using the model with those in the literature¹⁶ indicates that dispersion forces alone may be responsible for the thermophoretic behavior observed in ThFFF experiments. In fact, dispersion forces in organic solvents are typically an order of magnitude greater than the sum of all intermolecular forces in more polar solvents such as water,¹⁶ which is consistent with the reduced thermophoresis of polymers dissolved in such solvents.

The model does not allow the sign of the interaction constant to be determined from thermophoretic measurements; it may be positive or negative. However, a negative interaction constant would yield a mer–solvent interaction energy that is positive, in which case the polymer would not be dissolved by the solvent. An indirect indication of the sign of the interaction constant is given by the direction of polymer thermophoresis. ThFFF and other experiments indicate that the thermophoresis of polymers is always in the direction of the cooler region, which means that the Hamaker constant A in eq 33 is positive.

For polymers with high interaction constants, the quadratic term in eq 27 cannot be neglected. In such cases, the situation is more complex, especially for copolymers. Thus, the linear terms in eq 27 could be partially canceled in a solvent that is good for one kind of mer and bad for the other. In that case, the quadratic term could dominate and determine the thermophoretic behavior of the copolymer.

TABLE 4: Summary of Interaction Constants Calculated from Eq 33 Using Thermophoretic Mobilities Obtained from the Literature

solvent	dmonomer	
	styrene	methyl methacrylate
cyclohexane	$b_T = 0.66 \times 10^{-7} \text{ cm}^2/(\text{s}\cdot\text{K})$ $A = 3.24 \times 10^{-13} \text{ erg}$	
benzene	$b_T = 0.89 \times 10^{-7} \text{ cm}^2/(\text{s}\cdot\text{K})$ $A = 2.7 \times 10^{-13} \text{ erg}$	$b_T = 1.37 \times 10^{-7} \text{ cm}^2/(\text{s}\cdot\text{K})$ $A = 3.09 \times 10^{-13} \text{ erg}$
toluene	$b_T = 1.03 \times 10^{-7} \text{ cm}^2/(\text{s}\cdot\text{K})$ $A = 2.85 \times 10^{-13} \text{ erg}$	$b_T = 1.63 \times 10^{-7} \text{ cm}^2/(\text{s}\cdot\text{K})$ $A = 5.93 \times 10^{-13} \text{ erg}$
ethylbenzene ^a	$b_T = 0.95 \times 10^{-7} \text{ cm}^2/(\text{s}\cdot\text{K})$	
methylethyl ketone	$b_T = 1.39 \times 10^{-7} \text{ cm}^2/(\text{s}\cdot\text{K})$ $A = 1.65 \times 10^{-13} \text{ erg}$	$b_T = 1.48 \times 10^{-7} \text{ cm}^2/(\text{s}\cdot\text{K})$ $A = 1.85 \times 10^{-13} \text{ erg}$
tetrahydrofuran	$b_T = 1.0 \times 10^{-7} \text{ cm}^2/(\text{s}\cdot\text{K})$ $A = 0.45 \times 10^{-13} \text{ erg}$	$b_T = 1.3 \times 10^{-7} \text{ cm}^2/(\text{s}\cdot\text{K})$ $A = 3.6 \times 10^{-13} \text{ erg}$
ethyl acetate	$b_T = 1.16 \times 10^{-7} \text{ cm}^2/(\text{s}\cdot\text{K})$ $A = 2.61 \times 10^{-13} \text{ erg}$	

^a no data on thermal expansion coefficient for methyl methacrylate**TABLE 5: Summary of Polymer–Solvent Interaction Constants Calculated from Eq 35 Using Polymer–Polymer and Solvent–Solvent Interaction Constants from the Literature**

solvent	monomer	
	methyl methacrylate $A_{m-m} = 7.11 \times 10^{-13} \text{ erg}^{18}$	styrene $A_{m-m} = (6.37-9.8) \times 10^{-13} \text{ erg}^{17}$
cyclohexane	$A = 6.48 \times 10^{-13} \text{ erg}$	$A = \sqrt{A_{m-m}A_{s-s}}$ $A = (5.4-7.6) \times 10^{-13} \text{ erg}$ av: $6.5 \times 10^{-13} \text{ erg}$
$A_{m-m} = (4.64-5.9) \times 10^{-13} \text{ erg}^{19}$ ($1.15 \times 10^{-14} \text{ erg}^{18}$)		
benzene	$A = 5.96 \times 10^{-13} \text{ erg}$	$A = (5.6-7.0) \times 10^{-13} \text{ erg}$ av: $6.3 \times 10^{-13} \text{ erg}$
$A_{m-m} = 5.0 \times 10^{-13} \text{ erg}^{19}$		
toluene	$A = 6.25 \times 10^{-13} \text{ erg}$	$A = (5.8-7.3) \times 10^{-13} \text{ erg}$ av: $6.5 \times 10^{-13} \text{ erg}$
$A_{m-m} = (5.30-6.1) \times 10^{-13} \text{ erg}^{19}$		
methylethyl ketone	$A = 5.78 \times 10^{-13} \text{ erg}$	$A = (5.4-6.7) \times 10^{-13} \text{ erg}$ av: $6.1 \times 10^{-13} \text{ erg}$
$A_{m-m} = (4.53-4.7) \times 10^{-13} \text{ erg}^{19}$		
ethyl acetate	$A = 4.45 \times 10^{-13} \text{ erg}$	$A = (5.2-6.3) \times 10^{-13} \text{ erg}$ av: $5.8 \times 10^{-13} \text{ erg}$
$A_{m-m} = 4.17 \times 10^{-13} \text{ erg}^{19}$		

TABLE 6: Comparison of Polymer–Solvent Interaction Constants for Polystyrene Calculated Using Eq 35 and Polymer–Polymer and Solvent–Solvent Interaction Constants from the Literature with Values Obtained Using Eq 33 and Thermophoretic Mobilities from the Literature

solvent	Hamaker constant A for polystyrene ($\times 10^{-13} \text{ erg}$)	
	ThFFF data	eq 35 and refs 16–19
cyclohexane	3.2	5.4–7.6 (6.5)
benzene	2.7	5.6–7.0 (6.3)
toluene	2.9	5.8–7.3 (6.5)
methyl ethyl ketone	1.7	5.4–6.7 (6.1)
ethyl acetate	2.6	5.2–6.3 (5.8)

Summary and Conclusions

The model developed here for polymer thermophoresis takes a similar approach to that used in the model recently developed for suspended particles.⁶ Both models are based on the slip flow of liquid around the surface of a dilute component either dissolved or suspended in the liquid. The slip flow is induced by an osmotic pressure gradient, which is established by the temperature dependence of the solvent parameters. The difference between dissolved polymers and suspended particles lies in the source of the osmotic pressure gradient. With suspended particles, the osmotic pressure gradient is produced by a gradient in the concentration of dissolved solutes near the comparatively large particle surface. Without the dissolved solutes, the particle–solvent interaction constant in some solvents, such as water, is too small to produce a pressure gradient. This is consistent with laboratory measurements. Thus, it was found

experimentally that, in water,²¹ dissolved solutes are required to obtain measurable thermophoresis. In polymer solutions, the osmotic pressure gradient is produced solely by a gradient in the concentration of solvent molecules. The resulting slip flow is strong enough to induce thermophoresis of the mers in organic solvents where the interaction forces are large.

Because of the high concentration of solvent molecules and related excluded volume effects, a Boltzmann distribution in the concentration of solvent molecules around a mer cannot be established. Therefore, as the basis for the derivations that concentration distribution in surface layer, an assumption of small changes in the concentration and osmotic pressure is required. Using that assumption, the expression for the osmotic pressure can be made that contains only the monomer–solvent interaction potential and certain thermodynamic parameters of the solvent, which include the cubic coefficient of thermal expansion, the isothermal compressibility, and its temperature coefficient.

Next, a mathematical procedure developed for the theory of electrophoresis was used to obtain a general expression for the thermophoretic mobility. As the force potential responsible for the interaction between solvent molecules and mers, three dipole–dipole potentials, which are known to dominate in nonaqueous nonelectrolyte solvents, are considered. These potentials include the Keesom interaction between permanent dipoles, the Debye induction interaction between permanent and induced dipoles, and the London or dispersion interaction between spontaneously induced dipoles.

Using the dependence of these potentials on the distance between interacting objects (distance to the minus sixth power),

a general expression for polymer thermophoretic mobility was obtained that contains the value of the characteristic interaction constant. This Hamaker constant was calculated from the derived equation using thermophoretic measurements on polystyrene and poly(methyl methacrylate) in several organic solvents by ThFFF. Values of the interaction constants calculated in this way were compared with values from the literature. The values agree within an order of magnitude.

Dispersion forces must be invoked for polymer thermophoresis in organic solvents, since required values of the Hamaker constant are too high to be provided by other dipole–dipole interactions. Finally, to have measurable thermophoresis, the polymer should have a Hamaker constant calculated by theoretical methods that is at least 10–15 *kT*.

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