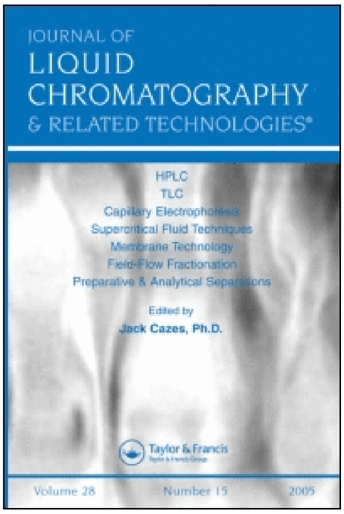
This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

# Surface Phenomena in Thermal FFF of Particles

S. N. Semenov[a]
[a] Institute of Biochemical Physics, Russian Academy of Science, Moscow, Russia

**To cite this Article** Semenov, S. N.(1997) 'Surface Phenomena in Thermal FFF of Particles', Journal of Liquid Chromatography & Related Technologies, 20: 16, 2687 — 2702
**To link to this Article: DOI:** 10.1080/10826079708005587
**URL:** http://dx.doi.org/10.1080/10826079708005587

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. LIQ. CHROM. & REL. TECHNOL., 20(16 & 17), 2687-2702 (1997)

# SURFACE PHENOMENA IN THERMAL FFF OF PARTICLES

S. N. Semenov

Institute of Biochemical Physics
Russian Academy of Science
117977, Moscow, Kosygin St. 4, Russia

## ABSTRACT

The theory developed in this article presents the physico-chemical mechanism of particle thermophoresis in a liquid. It is shown, too, that polarization phenomena may play an important role in thermophoresis. The possible role of polarization as the reason of the features observed experimentally in the experiments on ThFFF of particles and macromolecules is discussed.

## INTRODUCTION

One object of Prof. Giddings investigation for recent years was Thermal FFF of particles.[1-4] He also initiated my interest in this problem. As the result of our work, the paper[5] raised, where the principles of particle thermophoresis were explained using the general theory of the phoretic movement in liquids, which is presented in Ref. 6.

The main aim of our paper[5] was the explanation of metal particle thermophoresis, since it was the most obscure phenomenon observed by Prof. Giddings and Dr. Shiundu in their experiments. The possibility of thermophoresis for the metal particles was explained there. However, many details of the experimental data observed in Refs. 1-4 are still unexplained. This is the situation, which emphases the degree of originality and importance of these experiments. The unexplained features of particle thermophoresis can be formulated, roughly, as the following:

a) the particle thermophoretic mobilities depend on the particle size, while the theory developed in Ref. 5 does not predict such a dependence;

b) the particle thermophoretic mobilities increase as the salt concentration increases in the carrier liquid, while the theory developed in Ref. 5 does not predict such a dependence; and

c) different thermophoretic properties of the polymer particles and the polymer chains of the same chemical composition: in contrast to the particles, the thermophoretic mobilities of the polymer chains practically do not depend on the chain length and the salt concentration in the outer liquid.

The aim of this paper is to provide more a complete theory of thermophoresis in a liquid which may, at least qualitatively, explain the above-mentioned details observed in experiments.

There is a way to explain the above features of particle thermophoresis. It is the accounting of the surfactant concentration gradient along the particle surface, caused by its movement in thermophoresis. Due to the tangential transport of the surfactant ions or molecules in the particle surface layer, the exchange of surfactant should exist between this surface layer and the outer liquid to compensate the drain of the former and to maintain the stationary surfactant concentration.

This phenomenon, called *concentration polarization*, is known widely in the theory of particle electrophoresis.[8] Both electrophoresis and thermophoresis are related phenomena, which are surface-driven.[6-8] Since the concentration polarization plays an important role in electrophoresis, where it significantly changes the particle electrophoretic mobility, and where its degree depends on the particle size, we may hope that its role in thermophoresis also should be a significant one.

According to the current theory, the phoretic movement is due to the osmotic pressure gradient or the electrostatic force in the surface layer, where surfactant molecules or ions are accumulated. An electrostatic force acts on the non-compensated diffuse electric charge which exists in the double electric layers when the particle is suspended in an electrolyte. The osmotic pressure gradient may be due to both macroscopic temperature and surfactant concentration gradient. As a result, the "slipping" of the liquid in the surface layer arises, which leads either to particle phoresis or to the osmotic flow of the liquid, when the solid surface can not move. To derive the particle thermophoretic velocity we should solve four related mathematical problems:

a) derivation of the temperature distribution around the spherical particle in the outer constant temperature gradient;

b) derivation of the flow velocity profile in the surface layer;

c) derivation of the surfactant concentration distribution; and

d) derivation of the particle thermophoretic velocity.

To simplify the examination, we neglect the electric fields which may arise around the particle due to the concentration gradients of electrolyte, and examine the situation where the single type of the surfactant is accumulated in the surface layer with the concentration high enough.

## TEMPERATURE GRADIENT AROUND THE PARTICLE

This problem is discussed widely in the literature,[5,9] and we present, here, only the statement of the problem and the main results.

One supposes that the temperature distributions inside and outside a particle ($T_i$ and $T_e$, respectively) have the dipole form

$$T_i = \nabla T \cdot r \cdot \cos\vartheta \tag{1}$$

$$T_e = T_0 + \nabla_i T \cdot r \cdot \cos\vartheta + \frac{M_T}{r^2}\cos\vartheta \tag{2}$$

where $T_0$ is the temperature at the center of the particle, $r$ is the distance from its center, $\vartheta$ is the angle between the vector $\vec{r}$ and the outer temperature gradient $\nabla \bar{T}$, $M_T$ is the temperature "dipole moment" of the particle, and $\nabla_i T$ is the internal temperature gradient in the particle, which should be determined.

On the particle surface, at $r = R$, we have the boundary conditions

$$T_i = T_e \tag{3}$$

$$\theta_i \frac{\partial T_i}{\partial r} = \theta_e \frac{\partial T_e}{\partial r} \tag{4}$$

where $\theta_i$ and $\theta_e$ are the thermal conductivities of the particle and the external liquid, respectively. Expressions 1-4 give the complete picture of the temperature distribution. In further calculations, we need only the outer temperature distribution

$$T_e = \nabla T \cdot R \cdot \cos\vartheta \left( \frac{r}{R} + \frac{n-1}{n+2} \frac{R^2}{r^2} \right) \tag{5}$$

where

$$n = \frac{\theta_i}{\theta_e}$$

is the ratio of the thermal conductivities.

In the thin surface layer, where a significant osmotic pressure arises, we will use the coordinate $y = r - R << R$. According to Expressionn 5, in this thin layer, the temperature gradient can be written as

$$\nabla_\vartheta T = \frac{1}{R} \frac{\partial T}{\partial \vartheta} = -\sin\vartheta \frac{3\nabla T}{2+n} \left( 1 + n \frac{y}{R} \right) \tag{6}$$

Usually, the particles have thermal conductivities comparable to the liquids' (normal particles) or exceeding them significantly (metal particles).

## FLOW VELOCITY PROFILE IN THE SURFACE LAYER AND THE PARTICLE THERMOPHORETIC VELOCITY

The flow velocity profile in the thin surface layer is defined by the Navier-Stokes equations in the form[6-8]

$$\eta \frac{\partial^2 u_z}{\partial z^2} = \frac{\partial p}{\partial z} \tag{7}$$

$$\frac{\partial p}{\partial y} = -c(y,z)\frac{\partial \Phi}{\partial y} \tag{8}$$

where $\eta$ is the dynamic viscosity of a liquid, $u_z$ is its tangential velocity, $p$ is the pressure, $z = R \cdot \vartheta$ is the tangential surface coordinate, $c$ is the concentration of the of surfactant molecules dissolved in the liquid, and $\Phi$ is the surface potential of this surfactant molecule.

Equation 8 expresses the condition of the hydrostatic equilibrium across the surface layer. Near the particle surface, a quasi-thermodynamic equilibrium is also established, and the surfactant concentration distribution is the Boltzmannian one[6,7]

$$c(y,z) = c_{os}(y,z)e^{-\frac{\Phi(y)}{kT(y,z)}} \tag{9}$$

where kT is thermal energy and $c_{os}$ is the surfactant concentration at the distance y<<R from the particle surface, but, outside the surface layer. Equation 8, in combination with Expression 9, gives the excess pressure distribution in the surface layer

$$p = p_o + kTc_{os}\left(e^{-\frac{\Phi}{kT}} - 1\right) \tag{10}$$

where $p_o$ is the "outer" pressure in the liquid far from the particle.

Substituting the pressure distribution given by Expression 10 into Eqn. 7, we have equation

$$\eta\frac{\partial^2 u_z}{\partial y^2} = kT\frac{\partial c_{os}(R,z)}{\partial z}\left(e^{-\frac{\Phi}{kT}} - 1\right) + kc_o\frac{\partial T(y,z)}{\partial z}\left[e^{-\frac{\Phi}{kT}}\left(\frac{\Phi}{kT}+1\right) - 1\right] \tag{11}$$

Writing Eqn. 11, we assume that the longitudinal concentration and temperature gradients are too small to cause the changes of temperature and concentration comparable to their mean values. We also neglect the second powers and the mathematical products of the gradients. These assumptions are used in the further derivations, too. The boundary conditions to Eqn. 10 can be written as[6]

$$u_z = 0 \qquad \text{at } y=0 \tag{12}$$

$$\frac{\partial u_z}{\partial y} = 0 \qquad \text{at } y\to\infty$$

Using boundary conditions given by Expression 12, the flow profile in the particle surface layer can be written as

$$u_z(y,z) = \frac{kT}{\eta}\frac{\partial c_{os}(R,z)}{\partial z}\int_0^y dy'\int_\infty^{y'} dy''\left[e^{-\frac{\Phi(y'')}{kT}} - 1\right]$$
$$-\sin\vartheta\,\frac{3kc_o\nabla T}{\eta(2+n)}\int_0^y dy'\int_\infty^{y'} dy''\left(1+n\frac{y''}{R}\right)\left\{e^{-\frac{\Phi(y'')}{kT}}\left[\frac{\Phi(y'')}{kT}+1\right] - 1\right\} \tag{13}$$

where Expression 6 for the temperature gradient is used. The slipping velocity of the liquid in the whole surface layer can be written as

$$u_s = u_z(\infty,z) = -\frac{kT}{\eta}\frac{\partial c_{os}}{\partial z}\int_0^\infty y\,dy\left[e^{-\frac{\Phi(y)}{kT}} - 1\right] +$$
$$+\frac{3kc_o\nabla T}{\eta(2+h)}\int y\,dy\left(1+n\frac{y}{R}\right)\left\{e^{-\frac{\Phi(y)}{kT}}\left[\frac{\Phi(y)}{kT}+1\right] - 1\right\}\sin\vartheta \tag{14}$$

where integration by parts of Expression 13 is used. It is shown in Ref. 5 that the particle thermophoretic velocity $u_T$ and the slipping velocity (Expression 14), which can be written in the form

$$u_s = u_{s0} \cdot \sin\vartheta$$

are interconnected by the relationship

$$u_T = u_{s0} \tag{15}$$

The structure of the slipping velocity and thermophoretic velocity contains two terms corresponding to thermophoresis and diffusiophoresis in the concentration gradient due to the particle movement in the temperature gradient. This secondary concentration gradient may significantly change the movement of the particle. To derive it, we should formulate the appropriate equations.

## SURFACTANT CONCENTRATION DISTRIBUTION AROUND THE PARTICLE

If the thermophoretic movement of the particle is stationary and slow enough, the convection-diffusion equation for the surfactant concentration can be written in the form

$$\operatorname{div}\operatorname{grad} c_{os} = 0 \tag{16}$$

and its solution may be found as the "dipole" concentration distribution

$$c_{os}(r,\vartheta) = c_o + \frac{M_c}{r^2}\cos\vartheta \tag{17}$$

Expressions 16 and 17 are valid outside the particle surface layer. However, the equation expressing the stationary state of the surfactant concentration distribution in the stationary particle movement should be true, both in the particle surface layer and outside it. Such an equation can be written as

$$\operatorname{div}\vec{j} = 0 \tag{18}$$

where

$$\vec{j} = \vec{u} \cdot c - D \cdot \operatorname{grad} c \tag{19}$$

is the surfactant flux. Here, $D$ is the diffusion coefficient of the surfactant molecules and $\vec{u}$ is their velocity. If the particle surface layer is thin enough (the question "how much is thin?" will be discussed later), we can formulate the boundary condition to Eqn. 16 using Eqn. 19. As shown in Refs. 6, 7, 8, this boundary condition can be formulated as

$$D \frac{\partial c_{os}}{\partial r} \Big|_{r=R} = \operatorname{div} \vec{j}_s \tag{20}$$

where

$$\vec{j}_S = \int_0^{\infty} j_S \, dy \tag{21}$$

is the total excess transport of the surfactant in the surface layer and

$$j_S = \left( e^{-\frac{\Phi(y)}{kT}} - 1 \right) \left[ c_o u_z(y) - D \frac{\partial c_{os}}{\partial z} - \frac{D c_o}{T} \frac{\partial T}{\partial z} \frac{\Phi(y)}{kT} \right] \tag{22}$$

is the longitudinal excess flux of the surfactant in the particle surface layer.

Further, we will discuss the most interesting situation for ThFFF, where the surface potential well is deep enough and we can assume that

$$e^{-\frac{\Phi}{kT}} >> 1 \tag{23}$$

In this situation, we also can approximate the real potential distribution by expression

$$\frac{\Phi}{kT} \approx -\varepsilon_o \left( 1 - \frac{y}{h} \right) \tag{24}$$

where $\varepsilon_o$ is he depth of the surface potential well in *kT* units and *h* is its characteristic width. This assumption (Expression 23) and approximation (Expression 24), together with Expressions 13, 17 and 20-22, allow us to write the equation defining the concentration "dipole moment" $M_c$

$$-\frac{2M_c}{R^3} = -\frac{c_o kT}{\eta D}\frac{M_c e^{2\varepsilon_o}}{R^4}\int_0^\infty e^{-\varepsilon_o \frac{y}{h}} dy \int_0^y dy' \int_\infty^{y'} dy'' e^{-\varepsilon_o \frac{y''}{h}} -$$
$$-\frac{3kc_o^2 \nabla T e^{2\varepsilon_o}}{\eta(2+n)RD}\int_0^\infty e^{-\varepsilon_o \frac{y}{h}} dy \int_0^y dy' \int_\infty^{y'} dy'' e^{-\varepsilon_o \frac{y''}{h}}\left(1 + n\frac{y''}{R}\right)\left[1 - \varepsilon_o\left(1 - \frac{y''}{h}\right)\right] +$$
$$+\frac{M_c e^{\varepsilon_o}}{R^4}\int_0^\infty e^{-\varepsilon_o \frac{y}{h}} dy - \frac{c_o}{T}\frac{3\nabla T e^{\varepsilon_o}}{(2+n)R}\int_0^\infty e^{-\varepsilon_o \frac{y}{h}}\left(1 + n\frac{y}{R}\right)\varepsilon_o\left(1 - \frac{y}{h}\right) dy \tag{25}$$

After much algebra, this equation allows us to derive the concentration "dipole moment' as

$$M_c = \frac{3c_o k \nabla T R^3}{(2+n)T}\mathrm{Rel}\frac{\varepsilon_o - 1 + \frac{nh}{\varepsilon_o R}(\varepsilon_0 - 2) + 2\varphi\delta \cdot \mathrm{Rel}\left[2\varepsilon_o - 5 + \frac{nh}{\varepsilon_o R}(3\varepsilon_0 - 10)\right]}{2 + \mathrm{Rel} + 4\varphi\delta \cdot \mathrm{Rel}^2} \tag{26}$$

where the reduced parameters are introduced

$$\mathrm{Rel} = \frac{h e^{\varepsilon_o}}{\varepsilon_o R} \tag{27}$$

is the criterion of the concentration polarization degree of the particle,

$$\varphi = c_o \frac{4\pi d^3}{3} \tag{28}$$

is the volume fraction of the surfactant molecules or ions having the radius $d$; and

$$\delta = \frac{h \cdot R}{d^2} \tag{29}$$

is the parameter characterizing the ratio of the main sizes considered in the problem. Deriving Expression 26, we also used the known Stokes expression for the diffusion coefficient:

$$D = \frac{kT}{6\pi\eta d} \tag{30}$$

Besides the above mentioned parameters, Expression 26 also contains the parameter

$$\frac{nh}{\varepsilon_0 R} \tag{31}$$

which is small, when the particle/liquid ratio of the thermal conductivities is about 1, and it should be large for metal particles having high thermal conductivities. This parameter characterizes the role of the transverse temperature distribution in particle thermophoresis. We can consider these situations separately for the normal particles:

$$M_{cN} = \frac{3c_0 \nabla T R^3}{T(2+n)} \mathrm{Rel} \frac{\varepsilon_0 - 1 + 2\varphi \cdot \delta \cdot \mathrm{Rel}(2\varepsilon_0 - 5)}{2 + \mathrm{Rel} + 4\varphi \cdot \delta \cdot \mathrm{Rel}^2} \tag{32}$$

and for the metal particles:

$$M_{cM} = 3c_0 \frac{\nabla T}{T} R^3 \frac{h}{\varepsilon_0 R} \mathrm{Rel} \frac{\varepsilon_0 - 2 + 2\varphi \cdot \delta \cdot \mathrm{Rel}(3\varepsilon_0 - 10)}{2 + \mathrm{Rel} + 4\varphi \cdot \delta \cdot \mathrm{Rel}^2} \tag{33}$$

## DISCUSSION

Expressions 32 and 33 allow, after substitution into Expression 14, where Expression 17 is taken into account, to write the thermophoretic velocities for normal and metal particles

$$u_{TN} = \frac{3c_0 k \nabla T}{\eta(2+n)} \frac{h^2 e^{\varepsilon_0}}{\varepsilon_0^2} \left\{ 3 - \varepsilon_0 + \frac{\mathrm{Rel}\left[\varepsilon_0 - 1 + 2\varphi \cdot \delta \cdot (2\varepsilon_0 - 5)\mathrm{Rel}\right]}{2 + \mathrm{Rel} + 4\varphi \cdot \delta \mathrm{Rel}^2} \right\} \tag{34}$$

$$u_{\mathrm{T\ddot{U}}} = \frac{3c_0 k\nabla T}{\eta} \frac{h^3 e^{\varepsilon_0}}{\varepsilon_0^3 R} \left\{ 2(4-\varepsilon_0) + \frac{\mathrm{Rel}\left[\varepsilon_0 - 2 + 2\varphi\cdot\delta\cdot\mathrm{Rel}(3\varepsilon_0 - 10)\right]}{2 + \mathrm{Rel} + 4\varphi\cdot\delta\,\mathrm{Rel}^2} \right\} \tag{35}$$

At small values of criterion *Rel*, the thermophoretic velocities of both normal and metal particles are negative, i.e., particles should be driven to the cold wall of the FFF channel.

We can determine, roughly, the regimes of the thermophoresis with the concentration polarization as:

a) non-polarization regime, where

$\mathrm{Rel} \ll 1$;

b) first transition regime, where

$\mathrm{Rel} \cong 1$;

c) regime with the moderately large values of criterion Rel, where

$1 \ll \mathrm{Rel} \ll (4\varphi\cdot\delta)^{-1}$,

in this regime, as shown in the exact analysis of the Expressions 25 and 26, the convective transport of surfactant in the particle surface layer can be neglected as compared to the diffusional transport;

d) second transition regime, where

$\mathrm{Rel} \approx (4\varphi\cdot\delta)^{-1}$,

in this regime, both the convective and diffusion transport of surfactant in the particle surface layer are important;

e) regime of very large Rel values, where

$\mathrm{Rel} \gg (4\varphi\cdot\delta)^{-1}$,

in this regime, convective transport in the particle surface layer prevails.

Of course, the above classification is valid only at

$$4\varphi \cdot \delta << 1,$$

which condition seems to be true for the wide range of the experimental situations in FFF.[10]

The approximating expressions for the terms in the figure brackets of Expressions 34 and 35, which are designated as $f_N(\varepsilon_0, \delta, \varphi, \mathrm{Rel})$ and $f_M(\varepsilon_0, \delta, \varphi, \mathrm{Rel})$, correspondly, for the above mentioned regimes are represented in Table 1. The data represented in Table 1 show the transition from the negative thermophoresis at $\mathrm{Rel} << 1$ (no polarization, particles are driven to the cold wall) to the positive one at $\mathrm{Rel} \approx 1$ (moderate polarization, particles are driven to the hot wall). As criterion Rel increases, the isopolarization state may come on, where the particle thermophoretic velocity is equal to zero. For the normal particles, it occurs at

$$\mathrm{Rel}_i = \frac{\varepsilon_0 - 3}{\varepsilon_0 - 2} \qquad (36)$$

and for the metal ones, at

$$\mathrm{Rel}_{iM} = \frac{4(4 - \varepsilon_0)}{\varepsilon_0 - 6} \qquad (37)$$

Taking into account the range of validity for the approximation by Expressions 23 and 24, based on the assumption concerning the deep surface potential well, we can define the range of $\varepsilon_o$ values, where the isopolarization state is possible, for the metal particles, as

$$5 \leq \varepsilon_0 < 6 \qquad (38)$$

This is the range which is narrow enough, and we can suppose that metal particles should have the isopolarization state rather rarely. However, taking into account the large values of parameter $\varepsilon_o$, which are characteristic for metals,[10] the metal particles should be strongly polarized and they should be driven to the cold channel wall. In the experiments on ThFFF, where particles of different sizes made of the same material were analyzed, one can observe different situations represented in Table 1, since there are different particles

### Table 1

### Approximate Expressions for the Terms in the Figure Brackets of Expressions 34 and 35

| **Regime** | $\mathbf{f_N(\varepsilon_0, \delta, \varphi, Rel)}$ | $\mathbf{f_M(\varepsilon_0, \delta, \varphi, Rel)}$ |
|---|---|---|
| a) $Rel << 1$; | $3 - \varepsilon_0$ | $2(4 - \varepsilon_0)$ |
| b) $Rel \cong 1$ | $3 - \varepsilon_0 + \frac{(\varepsilon_0 - 1)Re}{2 + Rel}$ | $2(4 - \varepsilon_0) + \frac{(\varepsilon_0 - 2)Rel}{2 + Rel}$ |
| c) $1 << Rel << (4\varphi \cdot \delta)^{-1}$ | $2$ | $6 - \varepsilon_o$ |
| d) $Rel \approx (4\varphi \cdot \delta)^{-1}$ | See Exprn 34 | See Exprn 35 |
| e) $Rel >> (4\varphi \cdot \delta)^{-1}$ | $\frac{1}{2}$ | $\frac{6 - \varepsilon_0}{2}$ |

having the same parameters of the surface potential wall $\varepsilon_o$ and $h$ should have different values of criterion Rel corresponding to the size. If Expression 35 is valid, the behavior of the both metal and normal particles in the various polarization regimes should be similar. The main difference between the normal and metal particles is the factor $\frac{h}{\varepsilon_0 R}$ in the dependence of the thermophoretic velocity on the particle radius for the latter ones. As the particle size decreases, its thermophoretic velocity, which is negative at $Rel << 1$ increases up to zero at $Rel_i$, then it increases further with the size decrease up to transition to regime c), reaches the maximum and decrease in respect to this maximum in regime e). For metal particles with $\varepsilon_0 > 6$, the monotonous increase of the thermophoretic velocity modulus with the size decrease should be observed due to factor $\frac{h}{\varepsilon_0 R}$. Due to high values of the Hamaker constant for metals, just this dependence should be the most common one.

Since the ThFFF experiments are carried out with polymer and silica particles, which can be considered as the normal ones, we examine the normal particles in detail, in an attempt to explain the experimental data. The possible ranges of values for the parameters $\varepsilon_0, h, \delta, \varphi, Rel$ are discussed in Ref. 10, where the possibility of all the above mentioned polarization regimes is shown.

The experimental data of [Ref.1] show a nonlinear, slow increase of the ThFFF retention with the particle diameter. For the particles being the objects of the experiments reported,[1-4] the retention can be written as

$$Ret = \frac{Pe}{3} \tag{39}$$

where *Pe* is the transverse Peclet number

$$Pe = \frac{b_T \Delta T}{D_p} \tag{40}$$

$b_T$ is the particle thermophoretic mobility (thermophoretic velocity in the unit temperature gradient), $\Delta T$ is the temperature drop over the half-width of the channel, and $D_p$ is the particle diffusion coefficient, which depends on the particle radius as Expression 30 shows. Thus, the dependencies observed in [Ref. 1] correspond to a slow decrease of the particle thermophoretic mobility modulus with the increase of its size.

As Table 1 shows, such a dependence corresponds to regimes b), or d), where the modulus of the particle thermophoretic mobility increases with the particle radius. In the first case, the particle must have the Rel values lower than $Rel_i$. In principle, regimes b) and d) can be differentiated, if one knows whether particles are driven to the cold wall or to the hot one. However, we had not found such information in [Refs. 1-4].

The effect of the salt addition observed in [Ref.1] also may provide certain arguments pro regime b). The salt addition decreases the Debye length, which depends on the ion concentration $c_i$ as $c_i^{-\frac{1}{2}}$. In this way, the Rel values are decreasing too, and particles obtain higher thermophoretic velocity, either by transition into regime a) or into regime c), moving away from the isopolarization state. Also, the effect of the salt addition may be explained by the sharp increase in the surface potential due to ion's adsorption but, in this case, some new questions arise. In this number, one cannot explain why the particles and macromolecules of the same material exhibit so different thermophoretic properties. An explanation can be found if we assume that the "particles"-monomers, which comprise the polymer chain, are strongly polarized. Using the data of Table 1, and above-mentioned dependence of the width of the surface potential well in electrolytes, i.e., the Debye length, on the ion's concentration

$$h \approx c_i^{-\frac{1}{2}}$$

and assuming that the salt added to solvent is the strong surfactant, i.e., $c_o \approx c_i$, one can see that the thermophoretic velocity of the strongly polarized particle both in regimes c) and e) should not depend on the electrolyte concentration. In this way, the macromolecules move in the temperature gradient as a set of small, strongly porarized particles, interconnected by the elastic forces. However, these strongly polarized particles should be driven to the hot channel wall, while the most of the macromolecules are driven to the cold one. Among many others, this feature of the macromolecule thermophoresis needs further explanation.

The hypothesis discussed in [Ref. 2], where the effect of the salt addition is explained by the decrease of the particle-wall repulsion layer, should not be valid, because this effect must be important for both the particles and macromolecules, which have the same Debye screening layer and should have the same repulsion interaction with the wall.

## CONCLUSION

The theory developed shows the physico-chemical mechanism of particle thermophoresis in a liquid. It shows, too, that the polarization phenomena may play an important role in the thermophoresis. The polarization also may be the reason for the features observed experimentally in the ThFFF of particles and macromolecules.

## ACKNOWLEDGMENT

This work is supported by Russian Foundation for Base Research (Grant No. 95-03-08390a).

## REFERENCES

1. P. M. Shiundu, J. C. Giddings, J. Choromatogr. A, **715**, 117-126 (1995).

2. S. K. Ratanathanawongs, P. M. Shiundu, J. C. Giddings, Colloids and Surfaces, **105**, 243-250 (1995).

3. P. M. Siundu, E. E. Remsen, J. C. Giddings, J. Appl. Polymer Sci., **60**, 1695-1707 (1996).

4. P. M. Siundu, G. Liu, J. C. Giddings, Anal. Chem., **67**, 2705-2713 (1995).

5. S. N. Semenov, P. M. Siundu, J. C. Giddings, J. Colloid Interface Sci., **176**, 454-458 (1995).

6. J. L. Anderson, Anal. Rev. of Fluid Mech., **21**, 61-97 (1989).

7. S. S. Dukhin, **Electric Conductivity and Electrokinetic Properties of Disperse Systems**, Naukova Dumka Publ., Kiev, 1975. [In Russian]

8. V. G. Levich, **Physicochemical Hydrodynamics**, State Publishing of Physical and Mathematical Literature, Moscow, 1959. [In Russian]

9. L. D. Landau, E. M. Lifshits, **Mechanics of Continuous Media**, State Publishing of Technical and Theoretical Literature, Moscow, 1954. [In Russian]

10. S. N. Semenov, "Surface Phenomena in Sedimentation FFF," J. Liq. Chrom. & Rel. Technol., **20**, 2669-2685 (1997).

Received January 20, 1997
Accepted February 13, 1997
Manuscript 4349b