



Thermodiffusion and coupled phenomena / Thermodiffusion et phénomènes couplés

Thermodynamics of mass transport in diluted suspensions of charged particles in non-isothermal liquid electrolytes

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ARTICLE INFO

Article history:

Available online 19 April 2011

Keywords:

Non-equilibrium thermodynamics
Colloid particles
Electrolyte solution
Thermodiffusion

ABSTRACT

A thermodynamic theory is developed for the thermophoresis of dilute suspensions of charged colloid particles in electrolyte solutions. The calculation of relevant thermodynamic parameters using statistical mechanics is carried out in the Debye–Hückel approximation. The main experimental features observed for such systems are explained.

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1. Introduction

The thermodynamic approach to mass transport is based on the rate of entropy production Σ [1–5]:

$$\Sigma = \vec{J}_e \cdot \nabla \left(\frac{1}{T} \right) - \sum_{i=1}^N \vec{J}_i \cdot \nabla \left(\frac{\mu_i}{T} \right) \quad (1)$$

Here, \vec{J}_e is the energy flux, \vec{J}_i and μ_i are the material flux and chemical potential of the i th component, respectively, N is the number of components, and T is temperature. The energy flux and temperature profile are defined by the difference in temperature at the system boundaries, while the mass flux is defined by non-equilibrium thermodynamics as [1,2]:

$$\vec{J}_i = -n_i L_i \nabla \frac{\mu_i}{T} - n_i L_{iQ} \nabla \frac{1}{T} \quad (2)$$

where L_i and L_{iQ} are the Onsager coefficients, and n_i is the numeric volume concentration of the i th component.

In order to utilize Eq. (2) in a predictive capacity, it is transformed into a form that contains component concentrations and other physically measurable system parameters:

$$\nabla \mu_i = \sum_{k=1}^N \frac{\partial \mu_i}{\partial n_k} \nabla n_k - \bar{v}_i \nabla P + \frac{\partial \mu_i}{\partial T} \nabla T + e_i \bar{E} \quad (3)$$

Here P is the internal macroscopic pressure of the system, $e_i = -\frac{\partial \mu_i}{\partial \Phi}$ is the electric charge of the respective ionic particle, Φ is the macroscopic electric potential in the system, $\bar{E} = -\nabla \Phi$ is the electric field strength, and \bar{v}_i is the partial molecular volume, which is very similar in magnitude to the specific molecular volume v_i .

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Note that the partial derivatives in Eq. (3) are taken at constant values of the respective parameters, which are not parameters in the differentiation. Thus, the temperature derivative $\frac{\partial \mu_i}{\partial T}$ is calculated at constant pressure.

The thermodynamic approach utilizes the Gibbs–Duhem equation [1–5]:

$$\nabla P = \sum_{i=1}^N n_i \left(\sum_{k=1}^N \frac{\partial \mu_i}{\partial n_k} \nabla n_k + \frac{\partial \mu_i}{\partial T} \nabla T + e_i \vec{E} \right) \quad (4)$$

Eq. (4) defines the pressure gradient required to maintain hydrostatic equilibrium. Substituting Eq. (4) into Eq. (3), we obtain

$$\begin{aligned} \vec{j}_i = & -\frac{\phi_i L_i}{v_i T} \left[(1 - \phi_i) \left(\sum_{k=1}^N \frac{\partial \mu_i}{\partial \phi_k} \nabla \phi_k + \frac{\partial \mu_i}{\partial T} \nabla T + e_i \vec{E} \right) \right. \\ & \left. - \sum_{k \neq i}^N \frac{v_i \phi_k}{v_k} \sum_{l=1}^N \frac{\partial \mu_k}{\partial \phi_l} \nabla \phi_l + \frac{\partial \mu_k}{\partial T} \nabla T + e_k \vec{E} - (\mu_i + q_i) \frac{\nabla T}{T} \right] \end{aligned} \quad (5)$$

In formulating Eq. (5) we have introduced the volume fractions $\phi_i = n_i v_i$ and the heats of transport $q_i = L_{iQ} / L_i$ [1–5]. The volume fractions obey the equation

$$\sum_{i=1}^N \phi_i = 1 \quad (6)$$

The calculation of electric field strength in the system will be discussed later in relation to specific situations. Eqs. (5) and (6) are the complete set of equations describing mass transport in a stationary system. There is a problem related to these equations: for an N -component system, the number of the equations is $N + 1$, and one needs to make these equations mathematically consistent. Usually, it is assumed that one of the component fluxes is calculated in another way, and the respective Eq. (2) for that component is simply ignored. Usually, that selected component's material flux is calculated from the following equation for a closed system:

$$\sum_{i=1}^N \vec{j}_i = 0 \quad (7)$$

However, there is no reasonable way to select which component is calculated in this way, and as a result the physical properties of the system become dependent on this selection. To solve this problem for a binary system, an approach was suggested in Ref. [6]. In this work we extend that approach to multi-component systems.

2. Thermodynamics of mass transport

In order to eliminate the prediction by Eq. (5) of thermodiffusion mass transport in pure liquids, which is inconsistent with both the Gibbs–Duhem equation and the standard definition of the thermophoresis, we follow the approach used in Ref. [6] where the heat of transport is related to the chemical potential at constant volume by

$$q_i = -\mu_i \quad (8)$$

Using Eqs. (6) and (8), Eq. (5) can be written as

$$\vec{j}_i = -\frac{L_i}{T} \sum_k \frac{\phi_i \phi_k}{v_i} \left(\sum_{l=1}^N \frac{\partial \mu_{ik}^*}{\partial \phi_l} \nabla \phi_l + \frac{\partial \mu_{ik}^*}{\partial T} \nabla T - \frac{\partial \mu_{ik}^*}{\partial \Phi} \vec{E} \right) \quad (9)$$

where

$$\mu_{ik}^* = \mu_i - \frac{v_i}{v_k} \mu_k \quad (10)$$

and $-\frac{\partial \mu_{ik}^*}{\partial \Phi} = e_i - \frac{v_i}{v_k} e_k$. As follows from Eq. (10), $\mu_{ki}^* = -\frac{v_k}{v_i} \mu_{ik}^*$. We can write Eq. (7) in the form

$$\sum_{i=1}^N \vec{j}_i = -\sum_{i,k} \frac{(L_i - L_k) \phi_i \phi_k}{T v_i} \left(\sum_{l=1}^N \frac{\partial \mu_{ik}^*}{\partial \phi_l} \nabla \phi_l + \frac{\partial \mu_{ik}^*}{\partial T} \nabla T - \frac{\partial \mu_{ik}^*}{\partial \Phi} \vec{E} \right) \quad (11)$$

Because we cannot thermodynamically control the components' kinetic coefficients, Eq. (11) is consistent with Eq. (7) only in closed systems, where all the component fluxes are zero. In this case we can write an equation for the component material flux in the form equivalent to Eq. (9):

$$\vec{j}_k = \frac{L_k}{T} \sum_i^N \frac{\phi_i \phi_k}{v_i} \left(\sum_{l=1}^N \frac{\partial \mu_{ik}^*}{\partial \phi_l} \nabla \phi_l + \frac{\partial \mu_{ik}^*}{\partial T} \nabla T - \frac{\partial \mu_{ik}^*}{\partial \Phi} \vec{E} \right) \quad (12)$$

Eqs. (9) and (12) are distinguished by the terms containing the preset values of the respective material fluxes, and by the kinetic coefficients. For a system in which the two considered fluxes are equal to zero, Eqs. (9) and (12) will take the same form, and yield the same concentration distribution. Thus, Eq. (12) delivers no new information on such a system compared to Eq. (9), while the condition expressed by Eq. (8) allows the system of equations defined by Eq. (2) to be consistent for stationary systems when at least two of the components have material fluxes equal to zero. When such a condition is not fulfilled, the problem should be solved in another way. Ref. [6] outlined another way to solve the system in the case of a binary non-stationary and open system. In this paper, we discuss only those systems that are both stationary and closed.

Furthermore, we consider in this work the ternary system containing a neutral solvent with concentration ϕ_1 , an electrolyte salt dissociated into ions with concentrations $\phi_{\pm} = n_{\pm} v_{\pm}$, and isolated charged particles with concentration ϕ_2 , where ϕ_2 is so small that the charged particles make no contribution to the physicochemical parameters of the system. More specifically, we consider the thermophoresis of an isolated and charged colloid particle that is stabilized by an ionic surfactant. Usually, a symmetric electrolyte is used in such systems, where the numeric concentrations of the ions are equal to maintain electrical neutrality:

$$v_- \phi_+ = v_+ \phi_- \quad (13)$$

In such a system we can define the volume concentration of dissolved salt by $\phi_s = \phi_+ (1 + \frac{v_-}{v_+}) = \phi_- (1 + \frac{v_+}{v_-})$ and formulate the following approximate relationship in place of the more exact form expressed by Eq. (6):

$$\phi_s + \phi_1 = 1 \quad (14)$$

Here the volume contribution of charged colloid particles is ignored because their concentration is very low, that is, the condition $\phi_2 \ll \phi_s \ll \phi_1$ is assumed to be satisfied. The electric neutrality means that in our system, the ion concentrations are equal at any salt concentration and temperature. Consequently, the chemical potentials of the ions are equal: $\mu_+ = \mu_-$ (see Refs. [7,8]).

Using Eqs. (5)–(8) we obtain the equations for the material fluxes, which are set to be zero.

$$\vec{j}_2 = 0 = -\frac{\phi_2 L_2}{v_2 T} \left[\frac{\partial \mu_{21}^*}{\partial \phi_2} \nabla \phi_2 + 3 \frac{\partial \mu_{21}^*}{\partial \phi_s} \nabla \phi_s + \frac{\partial \mu_{21}^*}{\partial T} \nabla T + e_2 \vec{E} \right] \quad (15)$$

$$\vec{j}_- = 0 = -\frac{\phi_- L_-}{v_- T} \left(3 \frac{\partial \mu_{-1}^*}{\partial \phi_s} \nabla \phi_s + \frac{\partial \mu_{-1}^*}{\partial T} \nabla T - e \vec{E} \right) \quad (16)$$

$$\vec{j}_+ = 0 = -\frac{\phi_+ L_+}{v_+ T} \left(3 \frac{\partial \mu_{+1}^*}{\partial \phi_s} \nabla \phi_s + \frac{\partial \mu_{+1}^*}{\partial T} \nabla T + e \vec{E} \right) \quad (17)$$

where, $e_+ = -e_- = e$ (symmetric electrolyte). Index 2 is related to the colloid particles, index 1 to the solvent, and indices \pm to the respective ions. We will not write the equation for the flux of the background solvent \vec{j}_1 because it yields no new information in comparison with Eqs. (15)–(17), as outlined above. Solving Eqs. (16), (17), we obtain:

$$\nabla \phi_s = -\nabla T \frac{\partial(\mu_{+1}^* + \mu_{-1}^*)}{\partial T} \Big/ 3 \frac{\partial(\mu_{+1}^* + \mu_{-1}^*)}{\partial \phi_s} \quad (18)$$

$$2e \vec{E} = 3 \frac{\partial(\mu_{-1}^* - \mu_{+1}^*)}{\partial \phi_s} \nabla \phi_s + \frac{\partial(\mu_{-1}^* - \mu_{+1}^*)}{\partial T} \nabla T \quad (19)$$

Eq. (18) allows us to numerically evaluate the concentration gradient as

$$\nabla \phi_s \approx \phi_s S_T^s \nabla T \quad (20)$$

where $S_T^s \approx 10^{-3}$ is a characteristic value for salts with a typical concentration of 10^{-2} – 10^{-1} mol/L, that is $\phi_s \approx 10^{-4}$ or less. The maximal temperature gradient achievable in experiments is $\nabla T \approx 10^4$ K/cm. Substituting these values into Eq. (20) yields $\nabla \phi_s \approx 10^{-4}$ – 10^{-3} cm $^{-1}$. The same evaluation applied to parameters in Eq. (19) indicates that the first right-hand term in this equation can be neglected, and the equation for the thermoelectric power can be written as

$$\vec{E} \approx \frac{\partial(\mu_{-1}^* - \mu_{+1}^*)}{\partial T} \frac{\nabla T}{2e} = \frac{v_+ - v_-}{2e v_1} \frac{\partial \mu_1}{\partial T} \nabla T \quad (21)$$

For a non-electrolyte background solvent, the parameter $\frac{\partial \mu_1}{\partial T}$ can be evaluated as $\frac{\partial \mu_1}{\partial T} \approx \alpha_T kT$, where α_T is the thermal expansion coefficient of the solvent (Refs. [6,9]). In liquids the thermal expansion coefficient is typically low enough ($\alpha_T \approx 10^{-3}$ K $^{-1}$) that the thermoelectric field strength does not exceed 1 V/cm. This electric field strength corresponds to the

maximum temperature gradient discussed above. The electrophoretic velocity in such a field will be 10^{-5} – 10^{-4} cm/s. For a comparison, the thermophoretic velocity in such temperature gradients is usually at least ten to one hundred times higher.

These evaluations show that temperature-induced diffusiophoresis and electrophoresis of a charged colloid particle in a temperature gradient can be ignored, so that the expression for the Soret coefficient of a diluted suspension of the charged colloid particles can be written as

$$S_T^2 = -\frac{\nabla\phi_2}{\phi_2\nabla T} = -\frac{\partial\mu_{21}^{*p}}{\partial T} \bigg/ \phi_2 \frac{\partial\mu_{21}^{*p}}{\partial\phi_2} = -\frac{1}{kT} \frac{\partial\mu_{21}^{*p}}{\partial T} \quad (22)$$

Here superscript p refers to constant pressure and μ_{21}^{*p} is the combined chemical potential at constant pressure, which is defined as

$$\mu_{21}^{*p} = \mu_2^p - \frac{N_2 v_2^m}{v_1} \mu_1^p \quad (23)$$

where μ_1^p , μ_2^p are the chemical potentials of the respective components at constant pressure, v_1 and v_2^m are the specific molecular volumes of the solvent and the molecule or atom constituting the particle, respectively; N_2 is the number of internal molecules or atoms in the particle.

3. Microscopic calculations

Although the thermodynamic expressions for the Soret coefficient using parameter μ_{21}^{*p} were obtained by a number of the authors (e.g., see Refs. [1–5]), this approach is criticized in the literature. In Ref. [10], it is stated that the thermodynamic Soret coefficient should be proportional to a linear combination of the surface area and volume of the particle, as it contains μ_{21}^{*p} given by Eq. (23). Experiments show that the Soret coefficient is proportional to the particle size for colloid particles and is practically independent on particle size for molecular species. This is in agreement with predictions of the hydrodynamic theory. However, in Ref. [11] it is shown thermodynamically that this parameter is proportional to the osmotic pressure caused by the suspended colloid particles, which means that this problem requires additional study. Here, we apply a statistical mechanical approach to the calculation of the Soret coefficient.

In our calculations, we will use the fact that there is certain symmetry between the chemical potentials contained in Eq. (23). This symmetry, which was successfully used in Ref. [9], equates the term $\frac{N_2 v_2^m}{v_1} \mu_1^p$ with $N_1 \mu_1^p$, where N_1 is the number of solvent molecules that are displaced by the suspended particle. Equating the free energy as the sum of chemical potentials, we can say that $N_1 \mu_1^p$ is the chemical potential of the virtual colloid particle consisting of molecules of the liquid displaced by the suspended particle. For this reason, we can extend the results obtained in calculations of the chemical potential of the suspended particle μ_2^p to the calculation of parameter $N_1 \mu_1^p$ by a simple change of designations. We will consider the virtual particle containing N_1 uniformly distributed molecules of solvent interacting with molecules of the surrounding liquid solvent.

For an isolated particle placed in the liquid, the chemical potential at constant volume can be calculated using a modification of the following expression [12,13]:

$$\mu_2 = \mu_{02} + 4\pi \int_0^1 d\lambda \int_R^\infty \frac{g_{21}(r, \lambda)}{v_1} \Phi_{21}^*(r) r^2 dr \quad (24)$$

where R is the particle radius and r is the distance between a molecule of liquid and the center of the particle; $g_{21}(r, \lambda)$ is the pair correlative function, which expresses the probability of finding a molecule of liquid at \vec{r}_1 ($r = |\vec{r}_1|$) if the internal molecule or atom is placed at \vec{r}_2 ; and

$$\Phi_{21}^*(r) = \int_{V_{in}} \frac{dV_{in}}{v_2^m} \Phi_{21}(|\vec{r}_2 - \vec{r}_1|) \quad (25)$$

is the Hamaker potential used in colloid science [13,14] to study the interaction of colloid particles; and $\Phi_{21}(|\vec{r}_2 - \vec{r}_1|)$ is the respective intermolecular potential. The Hamaker potential is efficient at a distance of one molecular size, independent on the particle size. Parameter μ_{02} is the chemical potential of all non-interacting internal molecules or atoms that comprise the colloid particle. For colloid particles, μ_{02} plays no role, except maybe for heavy metal particles, although it can describe the isotope effect in molecular thermodiffusion (Ref. [9]). Parameter λ describes the gradual “switching on” of the interaction related to the considered particle. A detailed description of this representation can be found in Refs. [12,13].

The internal interactions within the particle can also contribute to its chemical potential, but according to basic principles of mechanics, such interactions cannot shift the barycenter, and are ignored in derivations related to kinetic effects such as thermodiffusion.

In a salt solution, the suspended particle interacts with both solvent molecules and ions. Both interactions can be described separately, as the salt concentration is usually very low and cannot change the solvent density to any significant

extent. The first kind of interaction, which is discussed in Refs. [6,9], uses the approximation $g_{21}(r, \lambda) = 1$ and the Hamaker interaction potential

$$\Phi_{21}^*(y) = -\frac{\varepsilon_{21} \sigma_{21}^3}{6 v_2^m} \left(\frac{1}{y} + \frac{1}{2+y} + \ln \frac{y}{2+y} \right) \tag{26}$$

where ε_{12} is the molecular energy of interaction, σ_{12} is the minimal molecular approach distance, $y = x/\sigma_{21}$, and x is the distance from the particle surface to the closest solvent molecule.

For electrostatic interactions, the properties of diluted systems may be used, where the pair correlative function has the Boltzmannian form (see Refs. [12,13]). Since there are two kinds of ions, Eq. (24) can be written as

$$\mu_2^e = -4\pi n_s \int_0^1 d\lambda \int_R^\infty (e^{\frac{\lambda \Phi_e}{kT}} - e^{-\frac{\lambda \Phi_e}{kT}}) \Phi_e(r) r^2 dr = -4\pi n_s kT \int_R^\infty (e^{\frac{\Phi_e}{kT}} + e^{-\frac{\Phi_e}{kT}} - 2) r^2 dr \tag{27}$$

where n_s is the numeric volume concentration of salt, $\Phi_e = e\varphi$ is the electrostatic interaction energy, and φ is the electric double layer potential around the charged particle.

The chemical potentials at constant pressure and volume for the suspended molecular or colloid particle can be related by expressing the forces acting on the particle at uniform and non-uniform pressure, respectively (Ref. [9]):

$$\nabla \mu_2^p = \nabla \mu_2 + \int_{V_{out}} \nabla \Pi dv \tag{28}$$

where Π is the local pressure distribution around the suspended molecule.

The local pressure distribution is widely used in hydrodynamic theory of kinetic effects in liquids [15–18], and is usually obtained from the condition of local mechanical equilibrium in the liquid. For electrostatic interactions, this equilibrium condition is written as $\nabla[(n_+ - n_-)\Phi_e(r) + \Pi] = 0$, where n_+ , n_- are the respective local distributions of ions. In Ref. [6] the local pressure distribution was used in the thermodynamic approach, and can be obtained through formulations for the condition of local equilibrium in a thin layer of thickness l and area S when that layer is shifted from position r to $r + dr$. This equilibrium condition can be expressed through the local conservation of specific free energy $F(r) = (n_+ - n_-)\Phi_e(r) + \Pi(r)$ for the isothermal system in such a shift. When this layer creates a closed surface around the particle, the change in free energy $(n_+ - n_-)\Phi_e(r)l dS$ due to the change in layer area dS should also be taken into account [9]. In the virtual shifting of a spherical layer, the change in volume is related to the change in the surface area by $dV = 2r dS$, and we obtain

$$\nabla[(n_+ - n_-)\Phi_e(r) + \Pi] + \frac{2(n_+ - n_-)\Phi_e(r)}{r} \vec{r}_0 = 0 \tag{29}$$

where \vec{r}_0 is the unit radial vector. The pressure gradient related to the change in surface area has the same nature as the Laplace pressure gradient discussed in Refs. [7,8]. Solving Eq. (29), in the assumption of a Boltzmann ion distribution [14], we obtain

$$\Pi = n_s kT (e^{\frac{\Phi_e}{kT}} + e^{-\frac{\Phi_e}{kT}} - 2) - 2n_s \int_\infty^r (e^{\frac{\Phi_e}{kT}} - e^{-\frac{\Phi_e}{kT}}) \frac{\Phi_e(r')}{r'} dr' \tag{30}$$

Substituting the pressure gradient calculated from Eq. (30) into Eq. (28), accounting Eq. (27), and considering the temperature-induced gradients related to the temperature dependence of the Boltzmannian exponents, we obtain the temperature derivative in the gradient of chemical potential for a charged colloidal particle, which is related to the electrostatic interactions in its electrical double layer

$$\frac{\partial \mu_2^{pe}}{\partial T} = \frac{4\pi n_s kR}{(n+2)} \int_R^\infty dr \int_\infty^r (e^{\frac{\Phi_e}{kT}} + e^{-\frac{\Phi_e}{kT}}) \frac{\Phi_e^2(r')}{(kT)^2} dr' \tag{31}$$

Here n is ratio thermal conductivities in the particle and solvent. For low potentials (i.e., $\frac{\Phi_e(r')}{kT} < 1$), where the Debye-Hueckel theory should work, Eq. (31) takes the form

$$\frac{\partial \mu_2^p}{\partial T} = \frac{4\pi n_s kR}{(n+2)} \int_R^\infty dr \int_\infty^r \frac{\Phi_e^2(r')}{(kT)^2} dr' \tag{32}$$

Using an exponential distribution for the electric double layer potential, characteristic for particles with low electrokinetic potential ζ , we obtain from Eq. (32)

$$\frac{\partial \mu_p^{2e}}{\partial T} = \frac{4\pi n_s k R \lambda_D^2}{(n+2)} \left(\frac{e\zeta}{kT} \right)^2 \quad (33)$$

where λ_D is the Debye length [7,13].

4. Results and discussion

Calculations of the non-electrostatic (Hamaker) terms, which are included in the thermodynamic expression for the Soret coefficient (Eqs. (17), (18)), are carried out in Ref. [9]. Combining these expressions with Eq. (33), we obtain the Soret coefficient of an isolated charged colloidal particle in an electrolyte solution:

$$S_T = \frac{4\pi n_s R \lambda_D^2}{T(n+2)} \left(\frac{e\zeta}{kT} \right)^2 + \frac{\pi^2 \alpha_T R \sigma_{21}^2 \varepsilon_{21} \sigma_{21}^3}{2(n+2) v_2^m k T v_1} \left(1 - \frac{v_2^m \sigma_{11}^5 \varepsilon_{11}}{v_1 \sigma_{21}^5 \varepsilon_{21}} \right) \quad (34)$$

Here α_T is the thermal expansion coefficient of the solvent, and σ_{11} , ε_{11} are the respective energetic parameters for the solvent.

The thermodynamic expression for the Soret coefficient contains terms related to the electrostatic interaction in the electric double layer and the Hamaker interaction of the suspended colloid particle. The electrostatic term has the same structure as the respective expressions for the Soret coefficient obtained by other methods using the same approximation [10,11,15,16]. In the Hamaker term, the last term in brackets reflects the effects related to displacing the solvent from volume occupied by the particle. These effects alone may cause a change in the direction of thermophoresis when the solvent is changed. However, such an inversion of thermophoresis can only occur when electrostatic interactions are relatively weak. When electrostatic interactions dominate thermophoresis, only positive thermophoresis can be observed. The relative role of the electrostatic mechanism can be evaluated by the parameter

$$n_s v_2^m \frac{\lambda_D^2}{\sigma_{21}^2} \frac{8}{\pi \alpha_T T} \frac{(e\zeta)^2}{\varepsilon_{21} k T} \frac{v_1}{\sigma_{21}^3} \left/ \left(1 - \frac{v_2^m \sigma_{11}^5 \varepsilon_{11}}{v_1 \sigma_{21}^5 \varepsilon_{21}} \right) \right. \quad (35)$$

A part of the physicochemical parameters contained in Eq. (29) is comparable for both mechanisms of thermophoresis. An exception is the characteristic length of interaction, which is much higher for electrostatic interactions. Also, the characteristic density of ions or molecules in the liquid, which govern electrostatic interactions with the colloid particle, is much lower than the density of the solvent molecules. The respective ratios are $\lambda_D^2/\sigma_{21}^2 \approx 10^3$ and $n_s v_2^m \approx \phi_s \approx 10^{-4}$ for typical ion concentrations in water. The parameter $1 - \frac{v_2^m \sigma_{11}^5 \varepsilon_{11}}{v_1 \sigma_{21}^5 \varepsilon_{21}}$ is small (about 0.1) when the colloid particles are compatible with the solvent. The characteristic ratio of the energetic parameters $\frac{(e\zeta)^2}{\varepsilon_{21} k T}$ is in the range 0.1–10. Combining these numeric values, one can see that the ratio given by Eq. (35) lies in the range 0.1–10 and is governed mainly by the value of the electrokinetic potential ζ .

5. Conclusion

Calculation of the ratio given by Eq. (35) shows that either the electrostatic or Hamaker mechanism can play a dominate role in thermophoresis at different values of the particle electrokinetic potential. When the Soret coefficient is large, particle thermophoresis is determined by electrostatic interactions, and takes a positive value. When the Soret coefficient is relatively small, thermophoresis is related to Hamaker interactions, and can have different directions in different solvents.

Together, the combination of the electrostatic and Hamaker interactions can explain a change in the direction of thermophoresis of charged particles where the Soret coefficient increases several times with the addition of salt and eventually becomes positive. An increase in the characteristic length of interaction with the surrounding liquid and the respective energy of those interactions are the main factors that contribute to the enhancement of particle thermophoresis with salt addition.

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