Soret Effect in Interacting Micellar Solutions

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We show that electrostatic effects have a dramatic influence on thermal diffusion of charged micelles. In the dilute regime, the Soret coefficient strongly decreases with the solution ionic strength, and scales as the square of the Debye-Hückel length. Yet, collective effects yield a reversed scenario even at fairly low surfactant concentration. We find that single-particle behavior can be explained using an interfacial tension mechanism proposed by Ruckenstein, which also fairly accounts for collective effects and opens the way to a general picture of thermal diffusion in disperse systems.

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The presence of a thermal gradient in a fluid mixture induces a relative matter flow of the components known as thermal diffusion or Ludwig-Soret effect [1]. This cross-flow effect plays a crucial role in many naturally occurring processes ranging from thermohaline convection in oceans [2] to component segregation in solidifying metallic alloys [3] or volcanic lava [4], and set the scene for giant fluctuations in nonisothermal mixtures [5]. Thermophoresis, a closely akin process consisting in the drift of dispersed particles due to a thermal gradient, can seriously affect semiconductor manufacturing and contribute to ambient pollution through airborne particle deposition [6,7]. Although known for a long time and clearly framed in terms of nonequilibrium thermodynamics concepts [8], the Soret effect still lacks, however, a general microscopic picture; and attempts to go beyond a phenomenological description have had thus far limited success. For instance, in most cases the denser component of a binary mixture diffuses towards the colder region (this is conventionally called *positive* Soret effect), but examples of reverse behavior are common, and no model is thus far able to give a general prediction of the direction of thermodiffusive motion. Some years ago, Ruckenstein [9] proposed an explanation of thermophoresis in dispersions based on an interfacial-tension driven mechanism. In this Letter, we show that charged colloidal dispersions represent a particularly fit system to test in a quantitative way the Ruckenstein model. We find that the model describes very well our experimental results, taking into account not only single-particle behavior, but also the effects of interparticle interactions. This opens the way to a general picture of thermophoretic effects in colloidal suspensions.

The mass flow J_m of a solute in the presence of thermal diffusion can be written as [8]

$$J_m = -d[D\nabla w - w(1 - w)D_T\nabla T], \tag{1}$$

where d is the material density of the solution, w is the mass fraction of the solute, D is the mass diffusion coefficient, and the phenomenological quantity D_T is called the coefficient of thermal diffusion. The ratio of thermal to “ordinary” diffusion is called the Soret coefficient $S_T = D_T/D$. It is also useful to introduce the thermal diffusion ratio $k_T = Tw(1 - w)S_T$, which is a pure number. Typical values of S_T range between 0.001–0.01 K^{-1} for gases or simple electrolytes [1], but can be several orders of magnitude larger for macromolecular and colloidal solutions.

After the seminal study by Giglio and Vendramini [10], thermal diffusion in complex fluids has been only marginally explored, outstanding exceptions being detailed studies of polymer solutions [11], where scaling concepts considerably help, and recent investigations of ferrofluids [12]. Here we present a detailed study of thermal diffusion in charged micellar solutions, showing that Ruckenstein’s model yields a *quantitative* prediction of the electrostatic contribution to S_T. We have chosen to work on micellar solutions of the ionic surfactant sodium dodecyl sulphate (SDS), whose equilibrium structural and dynamic properties have been studied at length in the past. In particular, SDS micelles are spherical aggregates of radius $R \approx 2.5$ nm, interacting via a standard DLVO potential [13]. We will show that thermal diffusion in SDS solutions has a very distinctive behavior. In the limit of very low concentration, S_T sensibly drops by adding salt. In other words, the single-particle Soret effect strongly increases with the electrostatic Debye-Hückel screening length. However, intermicellar interactions play a strongly conflicting role, to such an extent that even at moderately low SDS concentration the situation gets totally reversed, and S_T *increases* with increasing salt concentration.

We have used a simple but reliable experimental method first developed by Giglio and Vendramini [10], which exploits the deflection of a laser beam due to the concentration, and therefore refractive index gradient induced by the imposed temperature field. A schematic description of our apparatus is the following. The thermal diffusion cell is made of two horizontal closely spaced plates separated by a rectangular 5 mm thick optical-glass frame. Plates are thin gold-plated copper blocks, with milled grooves where the optical window is partially inserted to ensure good thermalization and avoid boundary convection. The variable compression of thin gaskets allows controlling, via an external gauge, plate parallelism and separation, which has been fixed to $h = 0.75$ mm. The cell has an optical path length of 40 mm and a sample volume of about 300 μl. The plate temperature is separately controlled by two Peltier elements, and a temperature difference $\triangle T \approx 0.5 - 1$ °C is imposed on a time scale of a few tenths of a second between the initially isothermal plates by cooling from the bottom. $\triangle T$ is then kept fixed within a few mK up to several hours. A He-Ne laser beam is mildly focused through the plate gap, and the transmitted beam position is monitored by a position-sensitive detector with a resolution of a few μm, placed at 60 cm from the cell.

The inset of Fig. 1 shows a typical beam deflection signal $\Delta z(t)$. The beam suffers first a very rapid downward deflection $(\Delta z)_{\mathrm{th}}$ due to the temperature dependence $\partial n/\partial T$ of the solvent refractive index, followed by a much slower change $\Delta z_S(t)$ due to thermal diffusion, eventually leading to a steady-state deflection $(\Delta z)_{th} + (\Delta z)_S$. The time dependence of the thermal diffusion contribution is given by

$$\Delta z_S(t) = (\Delta z)_S\left[1 - \frac{4}{\pi}\exp\left(-\frac{t}{\tau}\right)\right], \tag{2}$$

where $\tau = h^2/\pi D$. This expression is valid for $t > \tau/3$ [14]. For SDS micelles and the given plate spacing $\tau \approx 10^3$ s. The wide separation of time scales allows one to extract therefore both the dynamics and the steady-state value of the Soret effect. The thermal diffusion ratio is simply determined as

$$k_T = \frac{1}{T}\,\frac{\partial n/\partial T}{\partial n/\partial w}\,\frac{(\triangle z)_S}{(\triangle z)_{th}}, \tag{3}$$

where $\partial n/\partial w$ gives the concentration dependence of the refractive index. It is interesting to notice that Eq. (3) yields an internal calibration with no reference to the apparatus geometry once $\partial n/\partial T$ and $\partial n/\partial w$ are known.

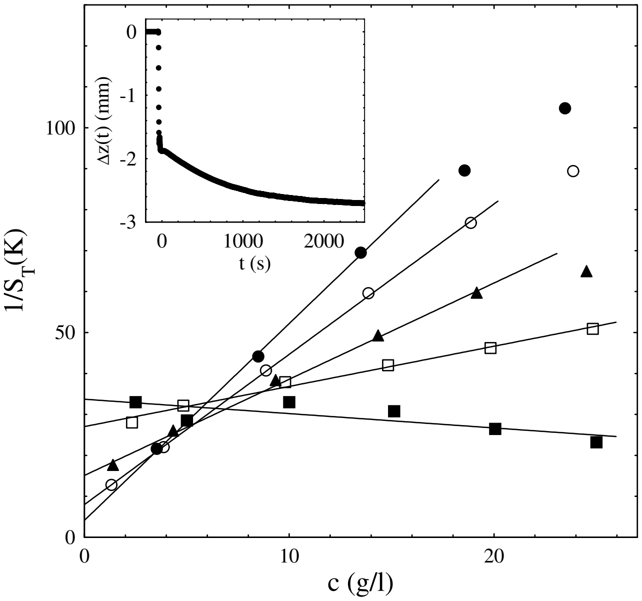

FIG. 1. Reciprocal Soret coefficient S_T^{-1} versus SDS concentration in the presence of 10 (●), 20 (○), 50 (▲), 200 (□), and 500 mM/l (■) added NaCl. Lines are fits to Eq. (4). Inset: Beam displacement for a 15 mg/ml SDS solution at 400 mM/l NaCl concentration.

We have studied thermal diffusion effects in SDS solutions at a fixed upper plate temperature of 25 °C by varying the surfactant concentration between 2.5–25 g/l (equivalent to $w = 0.25\%-2.5\%$, since SDS density is very close to 1 g/l) and the concentration c_S of added NaCl between 10 mM/l and 0.5 M/l. It must be noticed that SDS critical micellar concentration (cmc) is not totally negligible at low ionic strength, reaching up to 1.5 g/l at 10 mM/l NaCl. In the present Letter, we will always refer to the concentration c of SDS in micellized form, obtained for each value of c_S by subtracting from the total SDS concentration the cmc values reported in [15]. For each value of c_S, we found a reasonably wide concentration range where the Soret coefficient scales as the *reciprocal* of the micellar concentration. In Fig. 1, we show S_T^{-1} versus c for some values of c_S, fitting therefore its concentration dependence as

$$S_T^{-1} = S_{T0}^{-1}(1 + k_S c). \tag{4}$$

Figure 1 has the following two remarkable features.

(i) The intercept S_{T0}^{-1}, giving the single-particle behavior, grows more than tenfold by increasing the salt concentration from 10 to 500 mM/l. This means that the Soret coefficient increases very rapidly by reducing the ionic strength, and witnesses the dominant role of the electrostatic contribution to thermal diffusion.

(ii) Collective effects, however, strongly modify the dilute behavior. For instance, at 10 mM NaCl, S_T decreases fivefold by increasing SDS concentration from 0.5 to 2.5%. Since the intercept and slope of the fit show an opposite trend as a function of c_S, the dependence of S_T on the ionic strength actually reverses compared to the infinite dilution limit for $c > 10$ mg/ml.

To our knowledge, neither such a huge effect of the ionic strength on the Soret effect for charged colloids, nor the strong corrections due to interparticle interactions have thus far been reported.

We first discuss the single-particle behavior. Figure 2 displays the dependence of S_{T0} on the Debye-Hückel screening length $\lambda_{\mathrm{DH}} = \sqrt{\epsilon k_B T/[2e^2(c_S + cmc)]}$, and shows that S_{T0} grows approximately as λ_{DH}^2. In order to account for this scaling behavior, we recall that the electrostatic contribution to the interfacial tension between a charged colloidal particle and a solvent of dielectric constant ϵ is given, for low surface potential ψ_s, by $\gamma_{el} = -\epsilon\psi_s^2/8\pi\lambda_{\mathrm{DH}}$. Since λ_{DH} depends on T, a thermal gradient will induce an effective interfacial tension gradient $\nabla\gamma$ due to the unbalance of the electric stresses on the particle, which we shall assume to be the main source of thermophoretic motion. In simple words, we could say that particle redistribution takes place in order to minimize the interfacial free energy. This mechanism, which has been originally proposed by Ruckenstein [9], is closely related to thermocapillarity, that is, mass transfer due a temperature-dependent interfacial tension. More generally, Ruckenstein has shown that the stationary drift velocity U induced by an electric potential, ion concentration, or thermal gradient can be written in fairly general conditions as $U = -l\nabla\gamma/\eta$, where η is the viscosity of the solution and l is a characteristic length of the order of λ_{DH}. In particular, the "thermophoretic" velocity U_{T0} in the absence of interparticle interactions is found to be [9]

$$U_{T0} = -\frac{\epsilon\psi_S^2}{32\pi\eta T}\nabla T. \tag{5}$$

Unfortunately, this expression is valid only for small ψ_S. It is, however, well known that the Debye-Hückel linear approximation can describe many structural and dynamic properties of a colloidal suspension also for $\psi_S \gg k_BT$, provided that an effective charge Z_{eff} is used instead of the "bare" charge Z [17]. This is due to the fact that part of the counterions "recondense" in a thin layer of thickness δ near the particle surface, lowering the surface potential to values of the order of k_BT. Counterion condensation in micellar solutions has been numerically studied by Belloni [18], who found a layer thickness $\delta \approx 1$ nm for polyions of radius 2.5 nm, and experimentally tested for SDS micelles in [16]. We shall therefore assume that Eq. (5) can be maintained, provided that instead of Z we use the effective charge Z_{eff}. Using in this limit $\psi_S = Z_{\mathrm{eff}}e\lambda_{\mathrm{DH}}/\epsilon a^2$, where a is the particle size and e the unit charge, we have

$$U_{T0} = U_{\mathrm{NE}} - \frac{3\pi k_B Z_{\mathrm{eff}}^2 l_B \lambda_{\mathrm{DH}}^2}{4f_0a^3}\nabla T, \tag{6}$$

where $l_B = e^2/4\pi\epsilon k_BT$ is the Bjerrum length, $f_0 = 6\pi\eta a$ is the Stokes friction coefficient, and U_{NE} is a possible contribution to thermophoresis due to particle-solvent interactions of nonelectrostatic nature. The Soret coefficient can then be easily found by setting to zero the net particle flux $J = \rho U_T - D\nabla\rho$, where ρ is the particle number density. Using $D_0 = k_BT/f_0$ for the single-particle diffusion coefficient, we obtain therefore

$$S_{T0} = S_{\mathrm{NE}} + \frac{3\pi l_B Z^2}{4Ta^3}\lambda_{\mathrm{DH}}^2, \tag{7}$$

where S_{NE} is the ionic-strength independent term coming from U_{NE}. Equation (7) predicts therefore a dependence of S_{T0} on λ_{DH} which agrees with the observed scaling behavior. The amplitude of the quadratic term, evaluated by using the bare micellar radius and the effective charge value $Z_{\mathrm{eff}} \approx 17$ obtained in [16], is, however, more than twice the experimental value. On the other hand, if we include in the particle size the layer of condensed counterions by putting $a = R + \delta$ and use S_{NE} as the only free parameter, we get the full curve shown in Fig. 2, which closely fits the data. A sounder agreement might possibly be obtained by using recent calculations of U_{T0} from the full Poisson-Boltzmann equation, which take also into account effects due to the thermal conductivity mismatch between particle and solvent [19]. Unfortunately, analytical results can be found only in the limit of $\lambda_{\mathrm{DH}} = 0$.

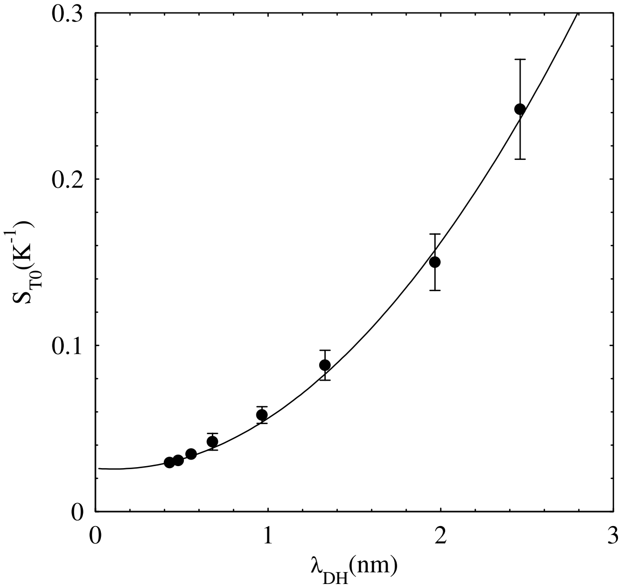

FIG. 2. Single-particle Soret coefficient S_{T0} as a function of the Debye-Hückel screening length. The full line is the prediction of Eq. (7)using the value of Z_{eff} obtained in [16], and including in the micellar radius the layer of condensed counterions.

The aforementioned model also yields some clues for an interpretation of collective effects. According to the data in Fig. 1, S_T decreases with c for $c_S \leq 0.4$ M/l, while the contrary happens for $c_S = 0.5$ M/l. Light scattering data for the osmotic compressibility $\partial\Pi/\partial c$ of SDS solutions show that micellar interactions switch from repulsive to attractive for $c_S \gtrsim 0.45$ M/l [13]. Therefore, an intuitive explanation of collective effects is that repulsive or attractive interactions, respectively, tend to hinder or favor the buildup of concentration gradients. Could this relation between S_T and $\partial\Pi/\partial c$ be more than qualitative? In order to account for interactions in the balance of diffusive fluxes, we can write the diffusion coefficient in a generalized Stokes-Einstein form: $D(\rho) = (\partial\Pi/\partial c)/f(\rho)$, where $f(\rho)$ is a concentration-dependent friction coefficient. The thermophoretic velocity at finite concentration, which we shall denote as U_T, will also change both because of hydrodynamic interactions and since the "thermocapillary" driving force could depend in principle on c. Having no hints about the latter contribution, we tentatively assume, however, that U_T is modified only through the *same* friction coefficient $f(\rho)$ as $U_T = U_{T0}f_0/f(\rho)$, which therefore cancels out when evaluating steady-state quantities. Taking into account the first order correction to the ideal behavior by writing $\partial\Pi/\partial c = k_BT(1 + 2B_2\rho)$, where B_2 is the second osmotic virial coefficient, this approximation immediately yields

$$S_T(\rho) = S_{T0}/(1 + 2B_2\rho), \tag{8}$$

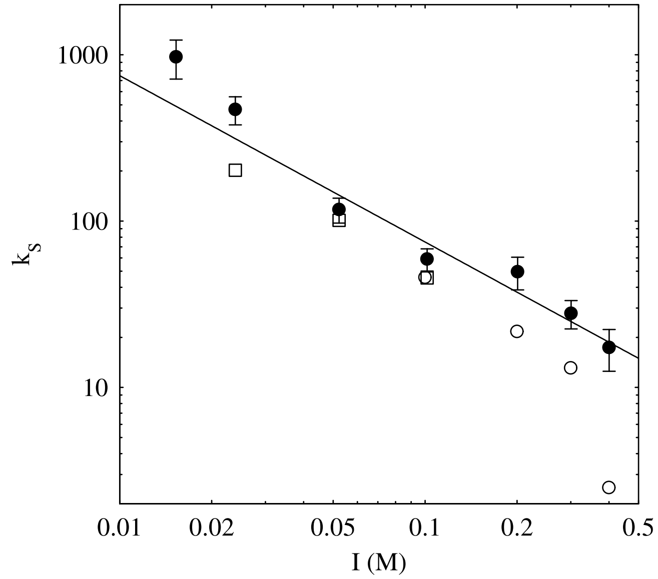

FIG. 3. Virial coefficient k_S versus solution ionic strength (●). The line is the best fit to $k_S = AI^{-1}$. Light scattering results for the virial coefficient of the osmotic compressibility from Ref. [13] (○), with a few additional points at lower ionic strength obtained in our lab (□), are shown for comparison.

meaning that the slope of the linear fit to the concentration dependence of S_T^{-1} should be simply given by $k_S = 2B_2$. The results for k_S are plotted in Fig. 3 as a function of the total ionic strength $I = c_S + cmc$, and compared to experimental virial coefficients for the osmotic compressibility obtained by light scattering. The logarithmic plot shows that, although numerically differing by an average factor of about 2, both quantities roughly scale as I^{-1}.

We do not fully discuss in this paper the transient behavior of the Soret effect, but we simply point out that the virial coefficients for the diffusion coefficient, derived from fits to Eq. (2), are in close agreement with the results by Corti and Degiorgio [13]. In particular, no specific scaling of S_T on D is found, at variance with what happens for polymer solutions [11], where the quantity $k_T D$ is roughly constant due to the predicted weak dependence of D_T on concentration [20].

Although still partially satisfactory, the simplified model we propose seems nonetheless able both to predict the correct scaling and order of magnitude of the electrostatic contribution to S_{T0}, and to include semiquantitatively the effects of interactions. We regard therefore Ruckenstein's suggestion as very promising. In particular, we find quite attractive the possibility of "translating" the effect of the thermal inhomogeneity of the solvent into an effective mechanical disturbance. This procedure could indeed be extended to particle-solvent interactions of a different nature. For instance, one could expect colloidal particles to move towards the hot plate whenever the interfacial free energy is a decreasing function of T. For specific solvation forces, this contribution (embodied in S_{NE}) could dominate, yielding a rationale for the occurrence of "negative" Soret coefficients.

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[1] J. V. Tyrrell, *Diffusion and Heat Flow in Liquids* (Butterworths, London, 1961).
[2] D. R. Caldwell and S. A. Eide, Deep-Sea Res. **32**, 965 (1985).
[3] L. L. Zheng, D. J. Larson, and H. Zheng, J. Cryst. Growth **191**, 243 (1997).
[4] R. T. Cygan and C. R. Carrigan, Chem. Geol. **95**, 201 (1992).
[5] A. Vailati and M. Giglio, Phys. Rev. E **58**, 4361 (1998).
[6] Y. Ye *et al.,* J. Aerosol. Sci. **22**, 63 (1991).
[7] W. C. Hind, *Aerosol Technology: Properties, Behavior, and Measurements of Airborne Particles* (UCLA School of Public Health, Los Angeles, 1982).
[8] S. R. D. Groot and P. Mazur, *Nonequilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
[9] E. Ruckenstein, J. Colloid Interface Sci. **83**, 77 (1981).
[10] M. Giglio and A. Vendramini, Phys. Rev. Lett. **38**, 26 (1977).
[11] K. J. Zhang *et al.,* J. Chem. Phys. **111**, 2270 (1999).
[12] E. Blums, S. Odenbach, A. Mezulis, and M. Maiorov, Phys. Fluids **10**, 2155 (1998).
[13] M. Corti and V. Degiorgio, J. Phys. Chem. **85**, 711 (1981).
[14] J. A. Bierlein, J. Chem. Phys. **23**, 10 (1955).
[15] D. Stigter, *Physical Chemistry* (Theorex, La Jolla, 1975), Chap. 12.
[16] S. Bucci, C. Fagotti, V. Degiorgio, and R. Piazza, Langmuir **7**, 824 (1991).
[17] S. Alexander *et al.,* J. Chem. Phys. **80**, 5776 (1984).
[18] L. Belloni, J. Chem. Phys. **99**, 43 (1985).
[19] K. I. Morozov, J. Exp. Theor. Phys. **88**, 944 (1999).
[20] F. Brochard and P.-G. De Gennes, C. R. Acad. Sci. II **293**, 1025 (1981).