

Experimental study on thermophoresis of colloids in aqueous surfactant solutions

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Abstract

Thermophoresis refers to the motion of particles under a temperature gradient and it is one of the particle manipulation techniques. Regarding the thermophoresis of particles in liquid media, however, many open questions still remain, especially the role of the interfacial effect. This work reports on a systematic experimental investigation of surfactant effects, especially the induced interfacial effect, on the thermophoresis of colloids in aqueous solutions via a microfluidic approach. Two kinds of commonly used surfactants, sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB), are selected and the results show that from relatively large concentrations, the two surfactants can greatly enhance the thermophilic mobilities. Specifically, it is found that the colloid–water interfaces modified with more polar end groups can potentially lead to a stronger thermophilic tendency. Due to the complex effects of surfactants, further theoretical model development is needed to quantitatively describe the dependence of thermophoresis on the interface characteristics.

Keywords: thermophoresis, thermal diffusion coefficient, SDS, CTAB, interface, microfluidics

(Some figures may appear in colour only in the online journal)

1. Introduction

Thermophoresis, also known as the Soret effect, denotes temperature gradient driven motion of particles or large molecules suspended in liquid media. The temperature gradient acts as a generalized force exerting on suspended particles and thus drives them either to the cold or to the hot regions. This is quite similar to what happens when an external driving force, such as an electric field, is applied. Since its discovery around 150 years ago, thermophoresis has been studied both theoretically and experimentally. It is a promising technique for particle and macromolecule manipulation and separation and some possible applications can be found in microfluidics [1] and bioscience [2, 3]. A host of experimental investigations have revealed some intriguing dependences of colloid thermophoresis (and negative thermophoresis) in aqueous solutions on particle concentration [4], particle size [5, 6], solution temperature [7, 8] and salinity concentration [9]. However, the underlying mechanisms are still under debate although

various theoretical models have been proposed to account for the above-mentioned experimental observations in recent years. For instance, Würger and coworkers [10–13] published a series of works on the hydrodynamic approach to model the thermophoresis of charged colloidal particles, involving the effects of dielectrophoretic force, thermo-osmotic pressure gradient and thermoelectricity. Using the thermodynamic approach, Duhr and Braun [5, 14] developed a thermophoresis model with the inclusion of entropy of ionic shielding and hydration effects.

From a microscopic viewpoint, thermophoresis can be regarded as an interface dominated phenomenon [15, 16]. It is our viewpoint that the most important and pioneering work owes to Ruckenstein [15] who exploited analogies between ‘phoretic’ movements of colloids and the Marangoni effect of droplets. Some other existing studies with special focus on this issue include Würger and co-worker’s theoretical treatments: on one hand, Würger [17] introduced the tangential surface force, i.e. Marangoni force, to take into account the

interface tension contribution. It was found that a larger interfacial energy would result in a larger tendency for the colloids to migrate to the warm region [17]. On the other hand, Morthomas and Würger [18] compared different boundary conditions on the surface of particles, i.e. slip or no-slip boundaries in their hydrodynamic model by using the slip length to reflect the change of particle surface properties. Experimentally, Ning *et al* [19] found an interesting inverse Soret effect for octadecyl group grafted silica colloidal particles in toluene solvent. This sign inversion may be attributed to the effects of surface coatings, like random swinging of octadecane molecules and position change of the shear plane [10].

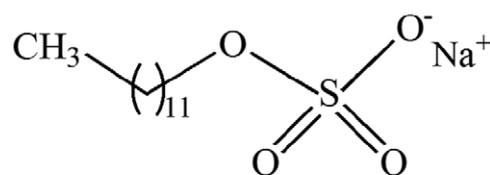
Despite the studies mentioned above, the existing literature still lacks systematic investigations on the interfacial effect, which may be regarded as one of the important origins of the interesting phoretic phenomena [16]. Getting a better understanding of this effect may eventually help us to take a step further towards uncovering the underlying mechanism of liquid thermophoresis. Surfactants were sometimes used to create the ‘model’ particle–solvent interface of colloidal solutions [6], owing to their adsorption onto the colloid surface. Consequently, the thermophoretic phenomena can be significantly altered and even sign reversal was observed [20]. By carefully adjusting the surfactant concentration, the interface properties of colloid–water may be continuously changed, and a systematic study of the interfacial effect can be realized. Thus, we present here a thorough experimental investigation of surfactant effects on the thermophoresis of highly dilute polystyrene (PS) colloidal particles in aqueous solutions under well controlled conditions. A recently developed microfluidic device [4] is utilized, allowing for generation of a linear temperature distribution. Besides the following discussion on surfactant effects, we also stress in particular that this study leads to a new means of using surfactants to control the thermophoretic phenomena in microfluidic applications.

2. Experimental section

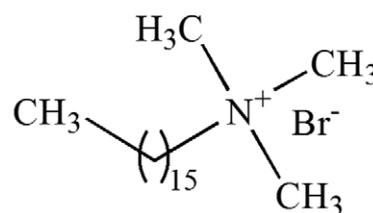
2.1. Sample preparation

The particles used in our thermophoresis experiments are two different groups of PS spheres. The first group purchased from Thermo Fisher Scientific Inc. is fluorescent particles of 0.72 μm , 2.0 μm and 4.8 μm in diameter, with a small amount of sulfate groups on the particle surfaces. It is stated by the manufacturer that ‘the surface of particles is very hydrophobic, with a low density of negatively charged surface ions to provide charge stabilization’ [21]. The second group is normal (non-fluorescent) 2.0 μm PS beads, purchased from EPRUI Nanoparticles & Microspheres Co. Ltd. These beads are surface-sulfonated [22], rendering them relatively hydrophilic. For convenience, the first group is termed GROUP 1, while the second is termed GROUP 2. Two commonly used ionic surfactants (with chemical structures shown in scheme 1), anionic sodium dodecyl sulfate, SDS ($M_w = 288.37 \text{ g mol}^{-1}$) and cationic cetyltrimethylammonium bromide, CTAB

A: SDS



B: CTAB



Scheme 1. Chemical structures of (A) SDS, (B) CTAB.

($M_w = 346.46 \text{ g mol}^{-1}$) purchased from Sigma-Aldrich (with a purity of $\geq 99\%$), were used without further purification.

Prior to the experiments, the original particle suspensions were centrifuged three times to wash off unknown impurities. Then the washed PS beads were resuspended with surfactant-DI water (Millipore Grade I) solutions to form desirable particle testing samples with particle volumetric fractions of about 0.00019% for 0.72 μm particles and 0.019% for the remaining larger particles. For such dilute particle suspensions, particle–particle interactions are negligible [4]. To ensure the homogeneity of testing samples, all the prepared particle samples were sonicated for about 15 min in an ultrasonic cleaner.

2.2. Experimental setup

The experimental setup is illustrated in figure 1. The core component is the microfluidic device, which consists of a stainless steel substrate with three channels on the front side. The middle channel, 400 μm wide, 35 μm deep and 20 mm long, is for loading the particle samples. The other larger channels on either side is for running hot and cold water streams so as to establish a transverse temperature gradient across the middle channel, and they both have the same dimensions: 2.0 mm wide, 1.5 mm deep and 20 mm long. The sample channel and the two hot/cold water channels on the front surface of the device are sealed with an optical adhesive film to form an enclosed space. Below the sample channel there is a cutting about 100 μm wide. It is directly exposed to ambient air to avoid heat transfer bypassing the sample channel (namely thermal energy leakage through the substrate of the sample channel). More details on this microfluidic device can be found in our previous work [4].

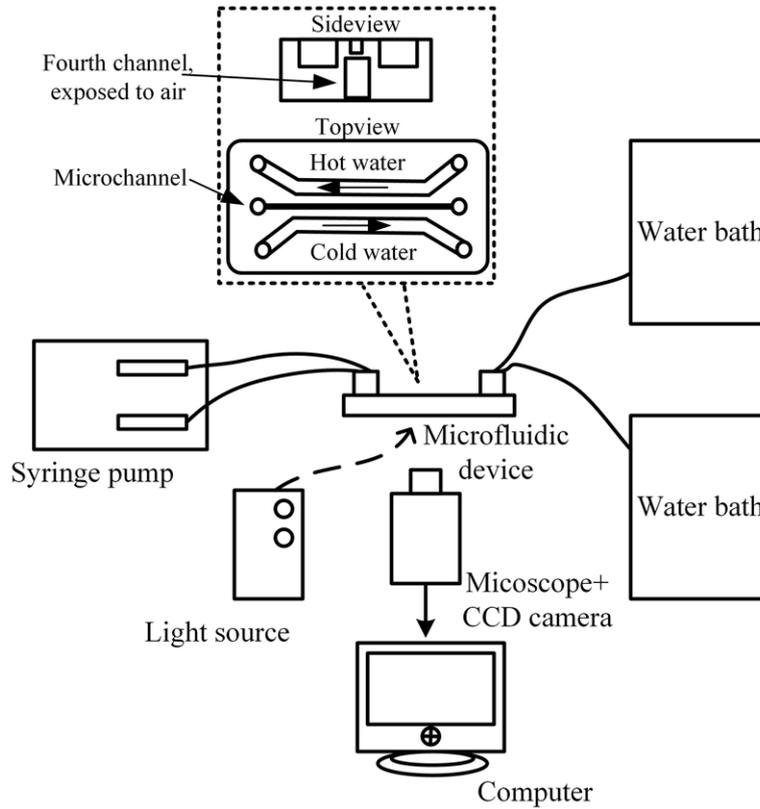


Figure 1. The experimental setup used for the thermophoresis study, including a stainless steel microfluidic device, two water baths, a dual-channel syringe pump, a light source, a microscope with a CCD camera, and a PC for collecting data. The inset inside the dashed rectangle presents a magnified view of the microfluidic device. The top view shows two larger channels for flowing hot/cold water streams and one smaller central channel for testing colloidal suspension samples. The side view shows a fourth channel, which is $100\ \mu\text{m}$ below the sample channel and directly exposed to ambient air. The counterflow mode (indicated by two opposite arrows) is utilized to produce linear temperature distribution along the transverse direction of the sample channel.

Additionally, the whole setup functions with other components: a dual-channel syringe pump set at a flow rate of 0.1ml s^{-1} is to suck hot and cold water streams from the hot and cold water baths, respectively. As shown in figure 1, the hot and cold water streams flow in opposite directions, resulting in a counterflow heat transfer mode. The temperatures of the two water baths were set to be $80\ ^\circ\text{C}$ and $5\ ^\circ\text{C}$, resulting in a linear temperature distribution from $48.3\ ^\circ\text{C}$ to $42.1\ ^\circ\text{C}$ across the middle testing channel with an average temperature of $45.2\ ^\circ\text{C}$ and a temperature gradient of about $1.55 \times 10^4\ \text{K m}^{-1}$. This transverse temperature distribution was measured by using a rhodamine B solution based thermometry method which relies on strong temperature-dependent fluorescent intensity and the detailed temperature measurement and characterization were reported elsewhere [4]. By measuring the temperature of two reservoirs (at the ends of sample channel) with thermal couples, the magnitude of the longitudinal temperature gradient was estimated to be two orders smaller than that of the transverse temperature gradient. Consequently, the thermophoretic motion of particles can only occur along the transverse direction. An inverted microscope is to observe the thermophoretic behavior of PS particles illuminated by a mercury lamp. Experimental images are to be captured with a CCD camera and then stored in a personal computer for later analyses.

3. Results and discussion

3.1. Effects of SDS/CTAB on colloid thermophoretic mobility

The single-particle tracking method [23] was employed to observe the thermophoretic motion of particles. In figure 2, the fluorescent $2.0\ \mu\text{m}$ particles of GROUP 1 are selected as a case to show the spatial distribution of an initial state (figure 2(a)) and the distribution at 30 min after commencing the experiments (figure 2(b)). To characterize the thermophoretic mobility, the thermal diffusion coefficient D_T is defined. A positive D_T indicates particle motion from hot to cold regions (i.e. thermophobic behavior), and a negative D_T denotes from cold to hot regions (i.e. thermophilic behavior). For each kind of particle sample, D_T is determined using

$$u_T = -D_T \nabla T. \quad (1)$$

Here, ∇T is the imposed temperature gradient and u_T is the thermophoretic velocity, obtained by measuring the distance traveled along the transverse direction for a single particle and then dividing it by the time elapsed. Over 400 measurements were averaged to eliminate the interference of Brownian motion. As shown in figures 2(a) and (b), almost linear displacement along the temperature gradient can be observed for the three labeled particles A, B and C. To ensure a two-dimensional (2D) thermophoresis study and

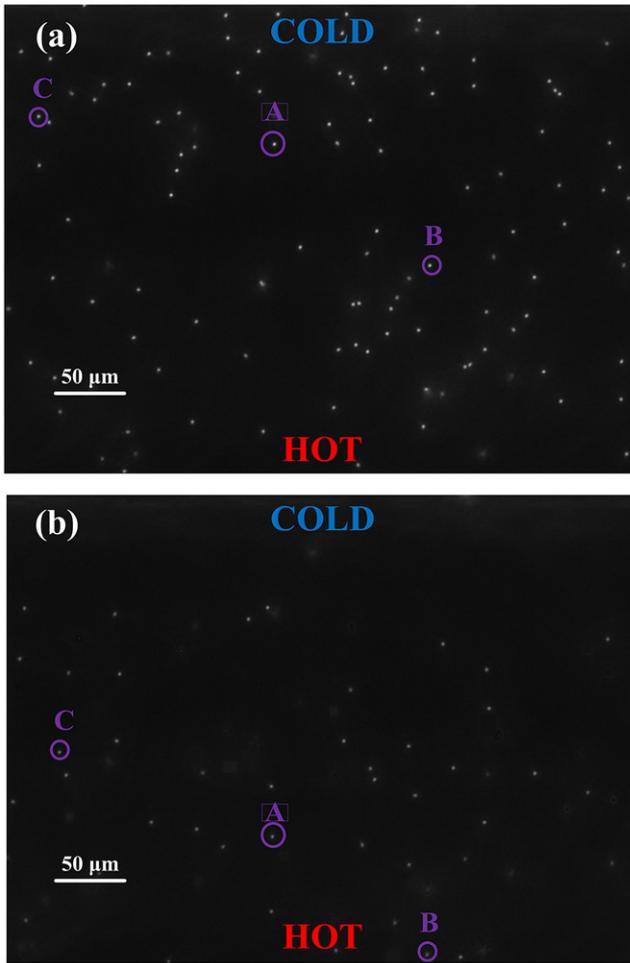


Figure 2. Spatial distributions of dilute 2.0 μm fluorescent particles dispersed in DI water. The cold side is at the top, while the hot side is at the bottom, resulting in a temperature gradient along the transverse direction of the microchannel. (a) The initial particle distribution and (b) the particle distribution at 30 min after commencing the experiment. ‘A’, ‘B’, ‘C’ label three different particles at initial time in (a) and at 30 min afterwards in (b).

avoid boundary effects, the focus plane of the microscope was adjusted to the middle plane of the microchannel. When PS colloids (density 1.05 g cm^{-3} , slightly larger than water) moved out of the field of view due to settling, their movements were no longer recorded. Besides, due to the very small channel depth of $35\ \mu\text{m}$, the possible free convection effect was negligible [24]. This is further evidenced by no noticeable difference in particle motion observed at different levels of the channel depth.

Prior to adding surfactants, the fluorescent particles with diameters of $0.72\ \mu\text{m}$, $2.0\ \mu\text{m}$ and $4.8\ \mu\text{m}$ in GROUP 1 were dispersed in DI water. Interestingly, exhibited different thermophoretic motion these three sized particles. The $0.72\ \mu\text{m}$ particles moved from the hot region to the cold region, exhibiting a thermophobic behavior which is similar to those results reported in the literature [5, 6]. The $2.0\ \mu\text{m}$ and $4.8\ \mu\text{m}$ particles, however, moved from the cold region to the hot region, showing a thermophilic behavior. Once the solvent was changed from DI water to SDS solutions with different concentrations, the results are depicted in figure 3.

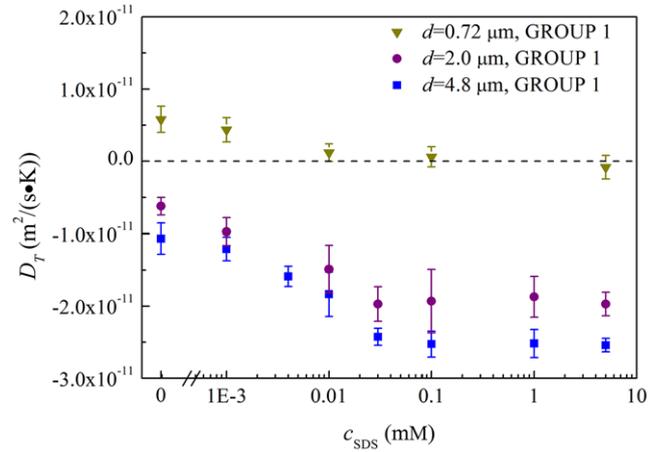


Figure 3. Variation of thermal diffusion coefficient D_T with SDS concentration c_{SDS} for $0.72\ \mu\text{m}$, $2.0\ \mu\text{m}$ and $4.8\ \mu\text{m}$ colloidal particles of GROUP 1, which are hydrophobic particles. The dashed line denotes $D_T = 0.0\ \text{m}^2\ (\text{s K})^{-1}$, dividing the data points into thermophobic and thermophilic regimes.

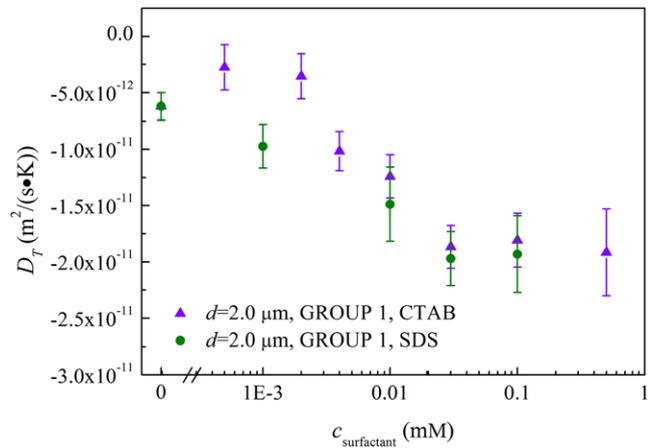


Figure 4. Variation of thermal diffusion coefficient D_T with SDS and CTAB concentrations for $2.0\ \mu\text{m}$ colloidal particles of GROUP 1.

SDS belongs to anionic surfactants and its critical micelle concentration (cmc) is around $8.7\ \text{mM}$ at $45\ ^\circ\text{C}$ [25] which is close to our experimental temperature. In our experiments, the surfactant concentration was always controlled below cmc. As shown in figure 3, D_T of the $2.0\ \mu\text{m}$ and $4.8\ \mu\text{m}$ particles, which move to the hot in DI water, becomes more negative with increasing SDS concentration (c_{SDS}), while for the $0.72\ \mu\text{m}$ particles, the positive D_T decreases when more SDS is added into the solution and even a small sign reversal can be observed at $c_{\text{SDS}} = 5\ \text{mM}$. All three samples show descending curves at small c_{SDS} , followed by a plateau around $0.03\ \text{mM}$. This suggests that an increase of SDS concentration causes more thermophilic tendency for all three sized particle samples.

Then, we changed the surfactant from anionic SDS to cationic CTAB, whose cmc is around $1.0\ \text{mM}$ at $45\ ^\circ\text{C}$ [26]. The results in figure 4 show that the thermophoretic behavior after adding SDS or CTAB for the $2.0\ \mu\text{m}$ particles is quite similar, except for a small difference. This happens when CTAB concentration is very small: D_T first increases (namely, absolute

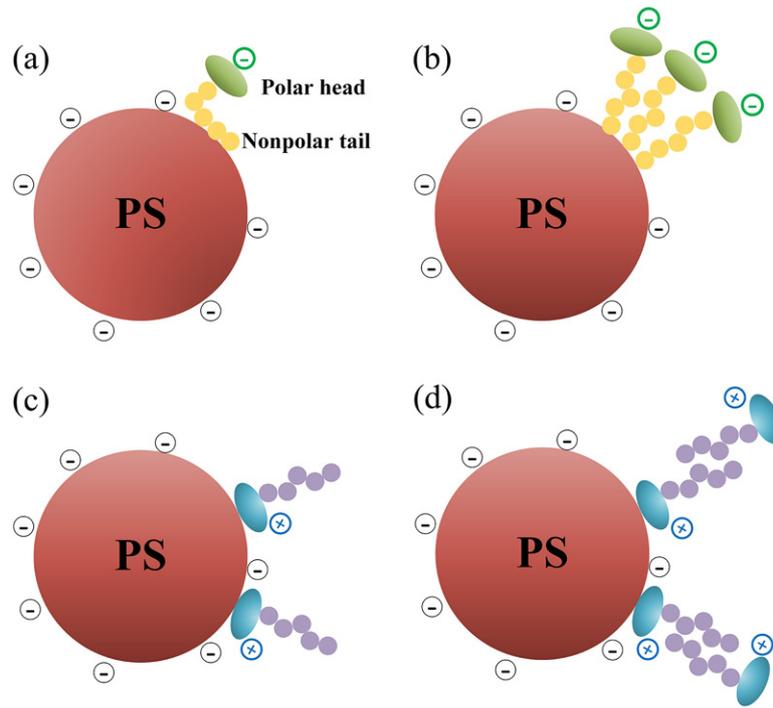


Figure 5. Schematic illustration of SDS adsorption. (a) At low concentration, the nonpolar tails of SDS molecules are in contact with the PS colloid surface with nonpolar tails mostly lying flat on the surface due to hydrophobic interaction; (b) at high concentration, the surfactant molecules align more vertically. Schematic illustration of CTAB adsorption. (c) At low concentration, the polar heads are in contact with the PS surface due to electrostatic interaction with nonpolar tails pointing outwards; (d) at high concentration, with charge neutralization on the colloid surface achieved, another layer of adsorption is formed due to hydrophobic interaction, with the polar heads of the second layer pointing outwards.

value decreases), being less thermophilic than the case in DI water, and then decreases as in the case of adding SDS. Very similar data points between those of adding SDS and CTAB at large concentrations (>0.01 mM) were obtained and a similar plateau also appeared when $c_{\text{CTAB}} = 0.03$ mM. Moreover, at 0.001 mM CTAB concentration, the suspension became unstable and the colloidal particles would soon drop to the bottom and D_T could not be obtained effectively. Despite different D_T values at low surfactant concentrations, for both SDS and CTAB surfactants with large enough concentration (~ 0.004 mM) and above (but still $< \text{cmc}$), one can always find a stronger thermophilic behavior than that in DI water.

3.2. Surfactant adsorption and interfacial effect on colloid thermophoresis

The influence of surfactants on colloid thermophoresis is an intriguing issue, while the principal impact may come from the predominant adsorption of the surfactant molecules onto the solid surfaces of colloids and the resulting change in interface property. For the anionic SDS and cationic CTAB surfactants used in our experiments, the adsorption processes are different. The DS^- and CTA^+ ions of SDS and CTAB molecules are both composed of nonpolar hydrocarbon tails (DS^- : $\text{CH}_3(\text{CH}_2)_{11}-$; CTA^+ : $\text{CH}_3(\text{CH}_2)_{15}-$) and polar heads (DS^- : $-\text{SO}_4^-$; CTA^+ : $-\text{N}(\text{CH}_3)_3^+$). Figures 5(a)–(d) are schematic illustrations showing the adsorption patterns. When SDS concentration is below its cmc, no matter how many SDS molecules are added, the polar heads would always point to

the bulk liquid side whereas the nonpolar tails are in contact with the surfaces of PS particles, with a primary driving force to be hydrophobic interaction [27] (figures 5(a) and (b)). The major difference is that at low SDS concentrations the SDS molecules would mostly lie flat on the colloid (figure 5(a)), while at high concentrations the SDS molecules would shift to a more vertical position due to sterically crowded PS surface (figure 5(b)) [27, 28]. For CTAB molecules, on the other hand, the charge is positive, opposite to that of the original PS surface. So at the first step, the polar heads would attach to the PS surface due to the electrostatic interaction, resulting in CTAB nonpolar tails pointing to the bulk liquid side (figure 5(c)). At the second step, with more CTAB molecules added and charge neutralization on the colloid surface achieved, another layer of adsorption would be formed with CTAB tails attached due to the hydrophobic interaction and heads of the second layer pointing to the bulk liquid [29] (figure 5(d)).

The above processes can also be verified from ζ -potential measurements for particles of volume fraction $\sim 0.1\%$ and at 45°C (close to the temperature of our thermophoresis experiment) by using a Malvern Nano Zetasizer (ZEN3600). Even at very low surfactant concentrations, e.g. ≤ 0.01 mM, the ζ -potential change is still obvious. Some literature works have reported that surfactant adsorption may happen at particle–liquid interfaces at relatively low concentrations [29–31]. It is seen that the ζ -potential is reduced with increasing SDS concentration, as shown in figure 6(a) (Similar trends can be observed for both $2.0\ \mu\text{m}$ particles of GROUP 1 and GROUP 2. The thermophoretic results of GROUP 2 will

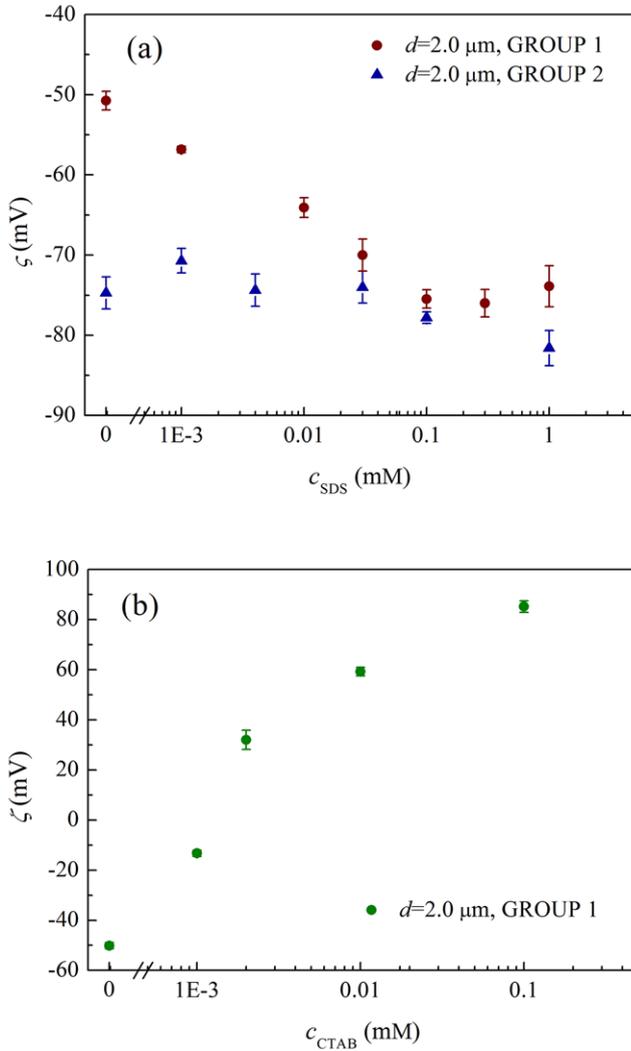


Figure 6. (a) Variation of ζ -potential with SDS concentration for 2.0 μm colloidal particles of GROUP 1 and GROUP 2; (b) variation of ζ -potential with CTAB concentration for 2.0 μm colloidal particles of GROUP 1.

be discussed later.) This is a consequence of increasing the number of polar head groups pointing outwards (from the colloid surface) with an increase of c_{SDS} . Meanwhile, figure 6(b) shows that the ζ -potential is negative at low CTAB concentrations, and then gradually changes to zero and finally becomes positive at certain high CTAB concentrations. The negative-to-positive transition of the ζ -potential is in accordance with the aforementioned two-step adsorption processes of CTAB. At 0.001 mM CTAB concentration, the absolute value of the ζ -potential is only around 13.3 mV, corresponding to a very unstable state and thereby giving rise to particle aggregation and even deposition to the bottom due to gravity as mentioned earlier. Thus, the measured D_T is not meaningful at this particular point and thus is not shown in figure 4. Nonetheless, the observed trend of our measured ζ -potential values for SDS and CTAB surfactants support our former described adsorption processes to some extent. In particular, the different dependences of the absolute value of ζ at low $c_{\text{SDS}}/c_{\text{CTAB}}$ indicate that the change of ζ is mainly due to DS^-/CTA^+ adsorption.

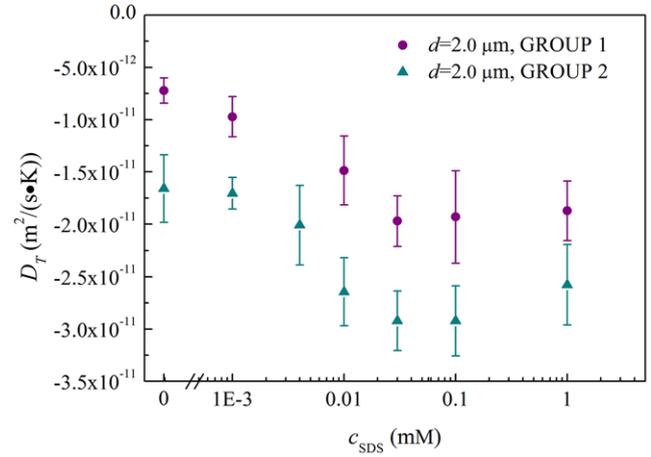


Figure 7. Variation of thermal diffusion coefficient D_T with SDS concentration for 2.0 μm colloidal particles of GROUP 1 and GROUP 2.

Because of adsorption, more surfactant polar head groups point toward the bulk liquid side, thereby making the colloid surfaces become more ‘hydrophilic’ and the whole dispersion system more stable. Comparing the adsorption processes and the thermophoretic results of SDS and CTAB surfactants, one can again find that the more surface-active colloid samples have larger thermophilic mobilities. This also explains the reason for the decrease in the absolute magnitude of D_T at low CTAB concentration (figure 4), which happens when more nonpolar hydrocarbon tails are pointing outwards. To further support this explanation, the 2.0 μm PS colloids of GROUP 2 were utilized. The surfaces of these colloids are sulfonated, covered by a large amount of polar end groups $-\text{SO}_3\text{H}$. In DI water, the particle sample of GROUP 1 yields a D_T value of $(-6.21 \pm 1.21) \times 10^{-12}$ $\text{m}^2 (\text{s K})^{-1}$, while the sample from GROUP 2 has $D_T = (-16.5 \pm 3.2) \times 10^{-12}$ $\text{m}^2 (\text{s K})^{-1}$. The latter one having a larger negative D_T coincides with the above observation. Moreover, these surface-sulfonated particles also show an increase of the thermophilic D_T with increasing c_{SDS} , similar to the particles of GROUP 1 (figure 7). The absolute values of D_T , however, are always larger for these surface-sulfonated particles at the same SDS concentrations.

The above experimental observations strongly support the relevance between the colloid–water interfacial electrostatic charge property and the thermophoretic results. There exists an approximate expression $\varphi_S = 3(d/R)\varphi$ (where d is the extended length of the surfactant, R is the particle radius and φ is the particle volume fraction) to estimate the required surfactant volume fraction φ_S for forming a fully saturated monolayer on the colloid surface [6]. Assuming the extended length d of SDS molecules as 1 ~ 2 nm, one can obtain φ_S of about 10^{-6} for the 2 μm -diameter colloids with $\varphi = 0.019\%$. As the mole mass and density of SDS are 288.37 g mol^{-1} and 1.01 g cm^{-3} , respectively, the corresponding SDS concentration can be estimated to be ~ 0.004 mM. (For the cationic CTAB, this theoretical value is doubled to be ~ 0.008 mM based on the same formulae for adsorption process.) It is then expected that above this value, the interface is standardized and D_T will remain unchanged as c_{SDS} is further

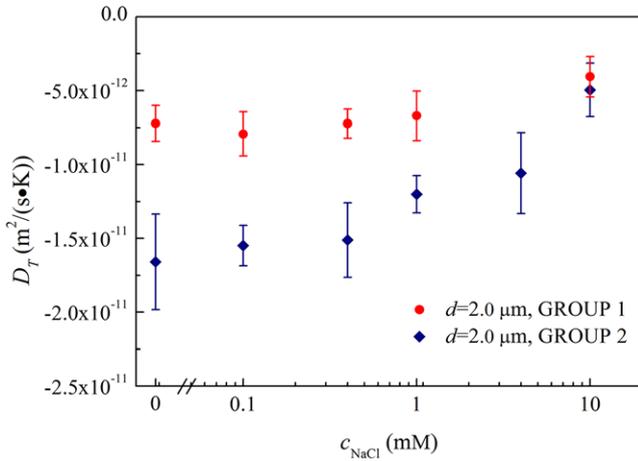


Figure 8. Variation of thermal diffusion coefficient D_T with NaCl concentration for 2.0 μm colloidal particles of GROUP 1 and GROUP 2 in the absence of any surfactants.

increased. The experimental results show a plateau reached around $c_{\text{SDS}} = 0.03 \text{ mM}$, larger than the theoretical prediction (figures 4 and 7). One may also expect the ζ -potential to remain unchanged when the saturated surface is achieved, and from figure 6(a) the plateau appears around 0.1 mM at $\varphi = 0.1\%$, once again larger than the theoretical concentration of $\sim 0.02 \text{ mM}$. The discrepancy may arise from the formation of a secondary layer of surfactants on the colloid surface [27].

3.3. Thermoelectric effect and other related issues

Along with adsorption onto the colloid surface, some non-adsorbed DS^- and CTA^+ remain in the bulk liquid. These ions and the free Na^+ and Br^- may cause thermoelectricity, which affects the thermophoretic phenomena together with surface modification due to surfactants. We accordingly try to distinguish this effect by adding electrolyte NaCl to the colloidal suspensions. In the absence of surfactants, no surface modification should have taken place and the effect of the electrostatic interaction on thermophoresis should play a major role here. The results in figure 8 show that D_T dependence on low salinity of 0–5 mM is very weak. Only a slight shift towards the thermophobic side (increase of negative D_T) can be observed as salinity increases. When c_{NaCl} is increased to 10 mM, only a few (3–4) colloids were found to be in the middle focus plane, while the remaining particles deposited to the channel bottom quickly. Thus we did not further increase the electrolyte concentration to obtain more data points. Various works have discussed the thermoelectric effect: For instance, Piazza and coworkers [32, 33] studied the coupled osmotic effect, collective effects and thermoelectricity on SDS micellar solutions. Würger and coworkers [12, 34] developed a theoretical model by relating the Soret coefficient to the heat of transport of ions, and the model can relatively well fit the experimental results of colloids at high ionic strengths. At low ionic strengths, our observed trend qualitatively agrees with that reported in [34]. Several studies suggested the dominate role of thermoelectric and specific-ion effects in thermophoresis [34, 35]. Here a question is to what extent

the thermoelectric and specific-ion effects affect the results of adding surfactant ions shown in figures 3, 4 and 7. Noting that the difference between the reduced Soret coefficients $\alpha_{\text{Na}} - \alpha_{\text{DS}} \approx 0$ ($\alpha_{\text{DS}} \approx 0.4 = \alpha_{\text{Na}}$) [36] is even smaller than $\alpha_{\text{Na}} - \alpha_{\text{Cl}} = 0.6$, when adding SDS surfactants one may expect a weaker thermoelectric effect than that of figure 8; it should be noted that the results of figure 8 exhibit quite a weak thermoelectric effect. Moreover, our earlier comparison shows that in DI water (without any surfactants or NaCl) the surface-sulfonated PS (GROUP 2) has markedly larger negative D_T than the normal PS (GROUP 1) has, and the influence of thermoelectricity due to additional free ions is not present under those circumstances. Thus, the strong thermophilic tendency at large surfactant concentrations observed in our experiments may be largely attributed to the colloid–water interface property.

To further interpret our experimental results, the following points should be noted.

- (1) Size dependence of the thermal diffusion coefficient D_T was observed. The larger sized particles show a stronger thermophilic tendency with or without surfactants. In fact, the size dependence of D_T is still a debated issue in existing literature studies. While Duhr and Braun [5] experimentally observed that positive D_T increases with particle size, Braibanti *et al* [6] showed in contrast that D_T is independent of particle size when the interfaces are standardized with surfactants. This contradiction has not been satisfactorily resolved, even though Morthomas and Würger [18] tried to reconcile them by modifying the previous size-independent theoretical model [11, 12] with a radius-related term arising from hydrodynamic slip. Our previous study on thermophoresis of both spherical and nonspherical colloids [37] reported size-dependent results, similar to those of the present work.
- (2) Similar to our previous published works [4, 37], our obtained negative thermophoresis values of micron-sized colloids (2.0 μm , 4.8 μm) at elevated temperature (45 $^\circ\text{C}$) in this study are different from numerous literature works. It is interesting to notice that the 0.72 μm colloids were found to move from the hot to the cold, in accordance with many other experimental results [5, 6, 8, 9]. This issue may be better interpreted together with the size dependence. Duhr and Braun [5] and Würger [17] separately derived a different model to account for the size dependence, and interestingly the two models lead to positive and negative D_T values, respectively. Both models introduce an interface-related term, i.e. hydration entropy [5] or surface tension [17], which actually supports our viewpoint that the interface plays an important role as our measured thermophoresis is found to change significantly with surfactant concentration. Thus, we believe that both the negative thermophoresis and size dependence result from colloid–surfactant solution interfacial effects. We found there are three ways to enhance the negative thermophoresis: (1) adding surfactants, which increases the polar end groups on PS colloids; (2) replacing the ‘hydrophobic’ PS (less polar groups, GROUP 1) with the ‘hydrophilic’ PS (more polar groups, GROUP 2); (3)

increasing the size of colloids from submicron to micron (i.e. size dependence).

- (3) Further attention is required to the interesting phenomenon of the general increase of thermophilic tendency with increasing surfactant concentration. Our above experimental results and adsorption analyses have provided strong evidence that when a colloid surface has more polar end groups, which renders the interface more ‘hydrophilic’, a larger thermophilic behavior can be observed. Unfortunately, no existing theoretical works can satisfactorily interpret this finding. Within the framework of an interfacial approach pioneered by Ruckenstein [15], it should be expected that the interface property plays a dominant role in determining thermophoretic phenomena. But a more rigorous theoretical treatment is needed to quantify the surfactant/colloid–solution interface interactions.
- (4) Although we propose our argument about the interface contribution to thermophoresis, we have to admit that adding surfactants does bring about a very complicated circumstance. The relevant surface adsorption and free ions-induced thermoelectricity have been discussed above. These two factors are nontrivial issues, considering the complex adsorption stages and the difficulty of getting the precise concentration for full surface coverage. Moreover, more subtle and still confusing issues may be involved, e.g. the pronounced increase of hydrodynamic radius of colloids with SDS adsorption, which is possibly due to colloid swelling as surfactant molecules diffuse into the particle interior [27]. These various influences of surfactants on thermophoresis come into play together, and thus it is difficult to clearly distinguish one from another. Although we paid special attention to the adsorption induced interfacial effect, which we indeed believe is a major contribution, other influences, especially the thermoelectricity; may contribute to our observed thermophoretic phenomena. Nevertheless, our experimental findings show strong ionic surfactant dependence of the thermophoretic mobility of colloids in aqueous solutions, whereas an intricate physical origin should be further investigated and more comprehensive models are needed.

4. Conclusions

In this work, we have carried out an experimental study to examine the surfactant effects on colloid thermophoresis. Direct visualization experiments were performed for dilute polystyrene (PS) colloids in aqueous surfactant solutions via a microfluidic approach. Two kinds of surfactants were used, anionic SDS and cationic CTAB, whose concentrations were chosen to be below cmc. The major thermophoretic results include: (1) increasing SDS concentration first leads to a monotonic increase of the thermophilic tendency, and then followed by a plateau D_T reached around 0.03 mM; (2) increasing CTAB concentration brings about (i) a thermophobic tendency, (ii) a similar trend of being more thermophilic, as that of adding SDS and (iii) a plateau value of D_T

in sequence. To interpret these results, we have analyzed the adsorption processes of these two particular surfactant molecules on the colloid surface. A qualitative correlation has been found between the thermophoretic phenomena and the interface properties such as the ζ -potential, showing that a more ‘hydrophilic’ interface, i.e. with more polar end groups, can lead to a stronger thermophilic tendency. Further evidence for the above observation was provided through two more experimental facts: First, the surface-sulfonated PS colloids have larger negative D_T than the normal PS colloids; and second, the thermoelectric effect induced by the free surfactant ions is suggested to be negligible by performing another independent study by adding NaCl. Despite the above analyses, we need to point out that the influences of surfactants on thermophoresis are very complex because some issues are not fully understood and further theoretical model development is needed to quantitatively describe the dependence of thermophoresis on the interface characteristics. To the best of our knowledge, this work is the first experimental study of using surfactants to alter the thermophoretic mobility and the first systematical experimental investigation of the related interfacial effect. As surfactant has proven itself a robust means to alter colloid thermophoresis, we may also anticipate it to be potentially useful in other interface-driven particle transport phenomena.

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