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Interaction between like-charged colloidal particles in aqueous electrolyte solution: Attractive component arising from solvent granularity

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The potential of mean force (PMF) between like-charged colloidal particles immersed in aqueous electrolyte solution is studied using the integral equation theory. Solvent molecules are modeled as neutral hard spheres, and ions and colloidal particles are taken to be charged hard spheres. The Coulomb potentials for ion-ion, ion-colloidal particle, and colloidal particle-colloidal particle pairs are divided by the dielectric constant of water. This simple model is employed to account for the effects of solvent granularity neglected in the so-called primitive model. The van der Waals attraction between colloidal particles, which is an essential constituent of conventional DLVO theory, is omitted in the present model. Nevertheless, when the electrolyte concentration is sufficiently high, attractive regions appear in the PMF. In particular, the interaction at small separations is significantly attractive and the contact of colloidal particles is stabilized. This interesting behavior arises from the effects of the translational motion of solvent molecules.

Key words: *colloidal particle, electrolyte solution, potential of mean force, integral equation theory, DLVO theory, solvent granularity*

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1. Introduction

The interaction between like-charged colloidal particles immersed in electrolyte solution is usually discussed using the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [1]. In this theory the interaction comprises the attractive van der Waals component W_{vdW} and the repulsive electric double layer component W_{edl}. $W_{\mathrm{vdW}}(r)$ is strong, where r is the distance between centers of colloidal particles, and it is almost independent of the ionic strength of the electrolyte solution. On the other hand, $W_{\mathrm{edl}}(r)$, which decreases almost exponentially with r, is strongly dependent on the ionic strength. As the electrolyte concentration increases, the electrostatic repulsion between colloidal particles is increasingly screened and the free-energy barrier for their cohesion becomes lower. In solution containing electrolytes (e.g., NaCl) at sufficiently high concentration (~ 0.1 M), aggregation of colloidal particles takes place.

In the DLVO theory, there is no attractive part except the term $W_{\mathrm{vdW}}(r)$, and the interaction between like-charged colloidal particles is purely repulsive if we neglect $W_{\mathrm{vdW}}(r)$. Here, we are concerned with the case where $W_{\mathrm{vdW}}(r)$ is absent in the model calculations. Kinoshita *et al.* analyzed the interaction between like-charged colloidal particles using the angle-dependent reference hypernetted-chain (RHNC) integral equation theory combined with a molecular model for water [2]. Though the term $W_{\mathrm{vdW}}(r)$ is not considered, attractive regions appear in some of the interactions calculated. This result suggests that an attractive component arises from a physical factor other than $W_{\mathrm{vdW}}(r)$. One of the essential differences between the DLVO theory and the analysis made by Kinoshita et al. is that the solvent granularity is taken into account in the latter.

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On the other hand, large particles immersed in small particles attract each other. Suppose that the number density of the small particles is much higher than that of the large particles, and the small and large particles are hard spheres, in other words, there are no soft interactions (e.g., van der Waals and electrostatic interactions) between the particles. In such a system, all the allowed system configurations have the same energy and the system behavior is of purely entropic origin. The presence of a large particle generates a volume from which the centers of the small particles are excluded. When two large particles contact each other, the excluded volumes overlap, and the total volume available to the translational motion of the small particles increases by this amount. This increase leads to a gain in the free energy of the small particles and an attractive interaction is thus induced between the large particles. In the original discussion by Asakura and Oosawa, the large particles are colloidal particles and the small particles are macromolecules [3,4]. Other studies [5–15] have considered solute molecules as the large particles immersed in small particles forming the solvent. In these studies the crucial importance of the solvent granularity and the translational motion of solvent molecules is emphasized.

In the present article, we analyze the interaction between like-charged colloidal particles in electrolyte solution using the integral equation theory. Solvent molecules are modeled as neutral hard spheres, and ions and colloidal particles are taken to be charged hard spheres. The Coulomb potentials for ion-ion, ion-colloidal particle, and colloidal particle-colloidal particle pairs are divided by the dielectric constant of water. This simple model is best suited to the exclusive investigation of the effects due to the solvent granularity, as opposed to the detailed but rather complicated model employed by Kinoshita et al.[2].

2. Model and theory

We consider a pair of colloidal particles immersed in a simple model of electrolyte solution which comprises neutral hard spheres and charged hard spheres corresponding to solvent molecules and 1-1 ions, respectively. The colloidal particles are modeled as like-charged hard spheres or uncharged (neutral) hard spheres. The Coulomb potentials between ion-ion, ion-colloidal particle, and colloidal particle-colloidal particle pairs are divided by 78.5, i.e., the dielectric constant of water. The potential parameters for ions are those developed by Pettitt and Rossky [16] and later modified by Kinoshita and Harano [17]. The solvent molecules and the colloidal particles are represented by "V" and "M" respectively. Major parameters for the pair potentials are summarized in table 1. The diameter of the solvent spheres is taken to be the effective diameter of water

Table 1. Partial charges and diameters of ions, solvent molecule[17], and colloidal particles. Q_j denotes the charge of particle j. σ_{jj} denotes the diameter of the hard-sphere interaction between particles of j. "V" and "M" denote the solvent molecule and the colloidal particles. Q_{M} is $-5, 0$, or $+5$.

Site	Q_j(e)	σ_{jj}(Å)
Na$^+$	1	2.26
K$^+$	1	3.14
Cs$^+$	1	3.72
Cl$^-$	-1	3.92
Br$^-$	-1	4.19
I$^-$	-1	4.54
V	0	2.80
M	Q_{M}	16.8

molecules $\sigma_{\mathrm{VV}} = 2.8$ Å. The diameter of colloidal particles is set at $\sigma_{\mathrm{MM}} = 6\sigma_{\mathrm{VV}} = 16.8$ Å. The pair potential is expressed as

$$u_{ij}(r) = \infty \qquad (r \leqslant \sigma_{ij}), \tag{1}$$

$$= \frac{Q_i Q_j}{78.5r} \quad (r > \sigma_{ij}), \tag{2}$$

where the usual mixing rule, $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ $(i, j = $ A, C, V, M), is employed and "A" and "C" denote anions and cations, respectively. Most of the calculations are carried out for $\phi_t = 0.383$ where $\phi_t = \Sigma_{l=A,C,V} \ \phi_l$, $\phi_l = (\pi\rho_l\sigma_{ll}^3)/6$, and ρ_l is the number density of l ($\phi_V = 0.383$ corresponds to $\rho_V = 0.033333$ Å^{-3} that is the number density of pure water at 1 atm and 298K).

Computer simulations are not practically applicable to systematic calculations when the size asymmetry of the particles is high. Moreover, they become much more difficult for a system including ions at finite concentration due to the problems arising from establishing estimations of the bulk equilibrium concentration of ions in each simulation. The integral equation theory we employ, however, is free from these considerable difficulties.

The ion-ion, solvent-ion, and solvent-solvent correlation functions for the bulk electrolyte solution are first calculated using the Ornstein-Zernike (OZ) equation [18]

$$h_{ij}(r) = c_{ij}(r) + c_{il}(r) * \rho_l h_{lj}(r), \tag{3}$$

coupled with the hypernetted-chain (HNC) closure[18]

$$h_{ij}(r) = \exp\left[-u_{ij}(r)/k_B T + h_{ij}(r) - c_{ij}(r)\right] - 1, \tag{4}$$

where $h_{ij}(r)$ $(i, j, l = $ A, C, V) is the total correlation function, $c_{ij}(r)$ is the direct correlation functions, ρ_i is the number density, k_B is the Boltzmann constant, $u_{ij}(r)$ is the pair potential, and * denotes the convolution product.

The interaction between colloidal particles is discussed in terms of the potential of the mean force (PMF) which is calculated from the correlation functions for the bulk electrolyte solution in the following manner. A colloidal particle is immersed in the solution, and the colloidal particle-solvent and the colloidal particle-ion correlation functions, h_{Mj} and c_{Mj}, are calculated using the OZ-HNC theory. The correlation function for colloidal particles $T_{MM}(k) = H_{MM}(k) - C_{MM}(k)$ is then calculated via

$$T_{MM}(k) = \sum_{l=A,C,andV} \rho_l H_{Ml}(k) C_{lM}(k), \tag{5}$$

where $T_{MM}(k), H_{Ml}(k)$, and $C_{lM}(k)$ are the Fourier Transforms of $t_{MM}(r)(= h_{MM}(r) - c_{MM}(r))$, $h_{Ml}(r)$, and $c_{lM}(r)$, respectively, and k is the wave number. The PMF $\Phi(r)$ is obtained as

$$\frac{\Phi(r)}{k_B T} = \frac{u_{MM}(r)}{k_B T} - t_{MM}(r), \tag{6}$$

where $u_{MM}(r)$ is the pair potential between colloidal particles. Equation (6) comes from the HNC approximation. Due to the presence of Coulomb potentials, care must be taken in the numerical treatment within the Fourier transformation. More details are described in earlier publications [19–24].

3. Results and discussion

3.1. Effects of electrolyte concentration on potential of mean force

Figure 1 shows the effects of electrolyte (NaCl) concentration on the PMF between like-charged colloidal particles ($\sigma_{MM} = 6\sigma_{VV}, Q_M = 5e$). The PMFs at smaller separations and at larger separations are plotted in figure 1(a) and in figure 1(b), respectively. The concentration tested is in the range from $1 \cdot 10^{-5}$ M to 1 M and ϕ_t is fixed at 0.383. Since the concentration of colloidal particles is zero due to the infinite dilution limit, the concentration of counter ions, which neutralize the charges of colloidal particles, is also zero. The concentration of counter charged ions, which screen the charges of colloidal particles, is equal to the electrolyte concentration. The curve for $1 \cdot 10^{-4}$ M is almost indistinguishable from that for $1 \cdot 10^{-5}$ M. This is because the electrolyte concentration is extremely low and the screening of the electrostatic repulsion is rather weak in these cases. However, adding more electrolytes to the solution leads to an increasingly stronger
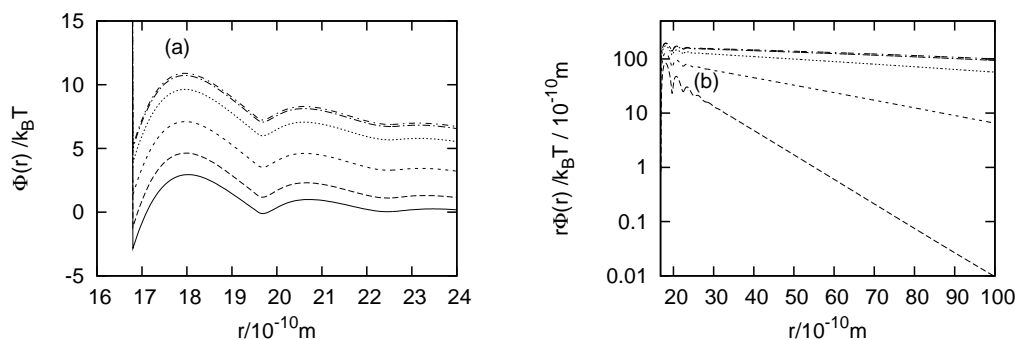
Figure 1. Potential of mean force between like-charged colloidal particles ($\sigma_{\mathrm{MM}} = 6\sigma_{\mathrm{VV}}, Q_{\mathrm{M}} = +5e$) immersed in our model electrolyte solution. The electrolyte is NaCl. Solid line: 1 M, Long-dash line: $1 \cdot 10^{-1}$ M, Short-dash line: $1 \cdot 10^{-2}$ M, Dotted line: $1 \cdot 10^{-3}$ M, Long dash-dot line: $1 \cdot 10^{-4}$ M, and Short dash-dot line: $1 \cdot 10^{-5}$ M. (a) Linear plot for smaller separations. (b) Logarithmic plot for larger separations. The solid line is omitted in (b).

screening. As the electrolyte concentration becomes higher, the PMF curve exhibits a downward shift (i.e., shifts in more attractive direction).

As shown in figure 1(a), the PMF curves exhibit an oscillation with a period corresponding to the diameter of the solvent molecules. When the electrolyte concentration is less than $1 \cdot 10^{-2}$ M, the PMFs are always repulsive and the colloidal particles should be dispersed. When the concentration is $1 \cdot 10^{-1}$ M, on the other hand, an attractive region appears in the immediate vicinity of the contact position and the contact value of the PMF is about $-1.18k_{\mathrm{B}}T$ (-0.70 kcal/mol). In the case of the 1 M solution, the contact value reaches $-2.85k_{\mathrm{B}}T$ (-1.69 kcal/mol) which is much larger than $k_{\mathrm{B}}T$. Therefore, the potential of mean force calculated for the present model qualitatively resembles that for the DLVO theory, with regard to the dependence on the electrolyte concentration, and a dimer of like-charged colloidal particles can be stabilized in spite of the absence of W_{vdW}, the attractive component in the DLVO theory. As for the PMFs at sufficiently large separations, the Poisson-Boltzmann picture is acceptable, because the curves plotted in figure 1(b) asymptotically approach straight lines [25]. Thus, the behavior of the PMF is similar to that predicted by the DLVO theory at a sufficiently large separation.
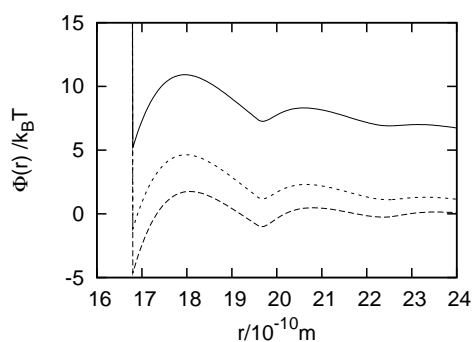

Figure 2. Line A (Long-dash): Potential of mean force between uncharged colloidal particles ($\sigma_{\mathrm{MM}} = 6\sigma_{\mathrm{VV}}, Q_{\mathrm{M}} = 0$) immersed in our model electrolyte solution (NaCl, $1 \cdot 10^{-1}$ M, $\phi_t = 0.383$). Line B (Short-dash): Potential of mean force between like-charged colloidal particles ($\sigma_{\mathrm{MM}} = 6\sigma_{\mathrm{VV}}, Q_{\mathrm{M}} = +5e$) immersed in our model electrolyte solution (NaCl, $1 \cdot 10^{-1}$ M, $\phi_t = 0.383$). Line C (Solid): Potential of mean force between like-charged colloidal particles ($\sigma_{\mathrm{MM}} = 6\sigma_{\mathrm{VV}}, Q_{\mathrm{M}} = +5e$) immersed in pure solvent ($\phi_t = 0.383$).

The PMF between uncharged colloidal particles is also calculated and shown in figure 2 as line A which is characterized by a large, negative contact value ($-4.63k_{\mathrm{B}}T$). This attractive behavior originates from the translational motion of solvent molecules. Line C in figure 2 illustrates the PMF between like-charged colloidal particles in pure solvent where there is no screening of the electrostatic repulsion by ions. Line C is similar to the long dash-dot and short dash-dot lines in figure 1. As the electrolyte concentration becomes higher, the PMF approaches line A with the oscillatory behavior qualitatively unchanged. The contact values of the PMFs for $1 \cdot 10^{-1}$ M (line B in figure 2), 1 M, and line A are, respectively, $-1.18k_{\mathrm{B}}T$, $-2.85k_{\mathrm{B}}T$, and $-4.63k_{\mathrm{B}}T$. It seems that the screening is not complete near the colloidal particle even when the concentration of electrolyte is 1.0 M.

A charge neutrality curve $q(r)$ for the charged colloidal particle is calculated to represent the screening in terms of the pair correlation function between the colloidal particle and the ion. The definition of $q(r)$ is

$$q(r) = Q_{\mathrm{M}} + 4\pi \int_0^r \sum_{i=\mathrm{A,C}} Q_i \rho_i g_{\mathrm{M}i}(r') r'^2 \mathrm{d}r', \qquad (7)$$

where r is the distance from the center of the colloidal particle, Q_i is the charge of i (i is the anion Cl^- and the cation Na^+), ρ_i is the number density of i, and $g_{\mathrm{M}i}(r)$ is the radial distribution function between the colloidal particle and i. The radial distribution function $g_{\mathrm{M}i}(r)$ is obtained using the OZ-HNC theory. The function $q(r)$ is shown in figure 3. It is clearly dependent on the electrolyte concentration, and the colloidal particle is increasingly covered by counter charged ions as the electrolyte concentration becomes higher.
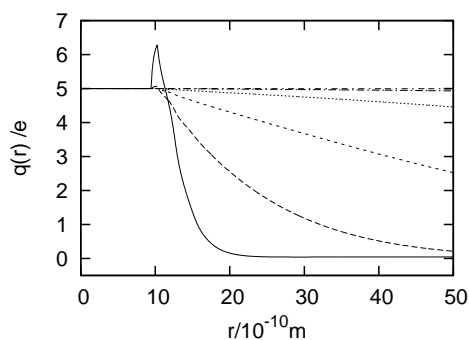

Figure 3. Charge neutrality curve $q(r)$ for the charged colloidal particle ($\sigma_{\mathrm{MM}} = 6\sigma_{\mathrm{VV}}, Q_{\mathrm{M}} = +5e$) immersed in our model electrolyte solution. The electrolyte is NaCl. Solid line: 1 M, Long-dash line: $1 \cdot 10^{-1}$ M, Short-dash line: $1 \cdot 10^{-2}$ M, Dotted line: $1 \cdot 10^{-3}$ M, Long dash-dot line: $1 \cdot 10^{-4}$ M, and Short dash-dot line: $1 \cdot 10^{-5}$ M.

This function shows the screening behavior for a colloidal particle caused by the electrolyte. For example, $q(r_1) = 0$ means that the charge of the colloidal particle is completely screened at r_1. The plot for 1.0 M shows that the colloidal particle charge is almost completely screened by ions at $r = 18.0 \cdot 10^{-10}$ m, and the distance is slightly larger than σ_{MM}. However, the colloidal particles are not completely screened when they contact each other in figure 1(a) and the attraction arising from the solvent molecules and ions is reduced.

Here, the plot for 1.0 M (the solid line in figure 3) has an interesting peak of about $q(r) = 6.2/e$ at around $10.0 \cdot 10^{-10}$ m, although there is no peak in other plots because of Coulomb repulsion between the cations (Na^+) and the positively charged colloidal particles. This peak means that the small cations (Na^+) contact the colloidal particle, even though the colloidal charge is also positive. This indicates that the anions (Cl^-) are positioned with the cations on the surface of the colloidal particle in the case of the high electrolyte concentration. Therefore, the cations are found in the first solvation shell of the colloidal particles. This phenomenon will be discussed in the next paper.

Based on the results described above, we draw the following conclusions. The behavior of the PMF between like-charged colloidal particles can be understood by the combination of the screened

repulsive electrostatic interaction and an attractive component originating from the translational motion of solvent molecules. When the concentration is less than $1 \cdot 10^{-2}$ M, the ion distribution roughly obeys the Poisson-Boltzmann picture and the Debye length is much larger than the size of solvent molecules. In this situation, two like-charged colloidal particles repulsively interact with each other through the electric double layer. On the other hand, when the concentration is larger than $1 \cdot 10^{-2}$ M, the Debye length is comparable or smaller than the size of solvent molecules. In this situation, the attractive component arising from the solvent granularity comes into play as the plot for $1 \cdot 10^{-1}$ M in figure 1(a). The addition of more electrolytes to the solution leads to stronger suppression of the electrostatic repulsion, making the attractive component more explicit.

3.2. Effects of ionic sizes on dimerization free energy of colloidal particles

It is known through experiments that the addition of electrolytes often causes a conformational transition of biopolymers. For a protein with many positively charged groups on the side chains, this addition induces a transition from an unfolded (fairly extended) conformation to a molten-globule-like conformation [26–28]. The ability to induce this transition is strongly dependent on anion species and follows, for monovalent anions, the order: $I^- > Br^- > Cl^-$ which is the reverse Hofmeister series. That is, for example, I^- is capable of inducing the transition at a lower concentration than Br^-. In the molten-globule-like conformation, the positively charged groups are close to one another, in marked contrast with the case of the unfolded conformation where they are fairly separated. Another interesting example is found in the DNA structural change which is known as the right-to-left (B-Z) transition of d[(G-C)] polymers and oligomers, induced by increasing the electrolyte concentration [29,30]. This structural transition, however, is strongly dependent on cation species and follows, for monovalent cations, the order: $Na^+ > K^+ > Rb^+ > Cs^+$ which is the Hofmeister series. A major geometric difference between B-DNA and Z-DNA is that the negatively charged phosphates are much closer together in Z-DNA. In the salting-out phenomenon observed for neutral proteins, the ability to decrease the solubility follows the orders $Cl^- > Br^- > I^-$ and $Na^+ > K^+ > Cs^+$.

Interactions between like-charged groups in biopolymers play an essential role in the conformational transition described above. In cases where the electrolyte concentration is very low, the biopolymers take the conformations in which the charged groups are well separated due to electrostatic repulsion. When the concentration becomes sufficiently high, the electrostatic repulsion is strongly screened, allowing the charged groups to come closer together. The salting-out phenomenon for neutral proteins, however, should be related to interactions between their uncharged groups: As these interactions become more attractive, protein aggregation should be promoted which leads to a decrease in protein solubility. For these reasons, the analysis of the effects of ionic species on the interactions between charged and uncharged colloidal particles gives physical insights into the behavior of biopolymers.

In the following treatment, we consider two sets of electrolytes: (i) NaCl, KCl, and CsCl; and (ii) NaCl, NaBr, and NaI to examine the effects of cation species and anion species, respectively, on the dimerization free energy $\Phi_{\min}/k_B T$, which is defined as the contact value of the PMF between two colloidal particles. The electrolyte concentration is chosen to be $1 \cdot 10^{-1}$ M. We consider colloidal particles with charges of $+5e$ and $-5e$ and those without charges.

First, we fix ϕ_t at 0.383. The relation between $\Phi_{\min}/k_B T$ and the cation species and that between $\Phi_{\min}/k_B T$ and the anion species are illustrated in figure 4(a) and (b), respectively. It is observed that $\Phi_{\min}/k_B T$ for colloidal particles with negative charges is considerably dependent on the cation species while no significant dependence on the ionic species is clear in the other cases. In particular, the addition of Na^+ leads to a much larger, negative value of $\Phi_{\min}$ than K^+ and Cs^+. On the other hand, $\Phi_{\min}/k_B T$ for positively charged colloidal particles is relatively independent of the anion species. This result can be understood in the following way: Firstly, small counter-charged ions can get closer to the colloidal particles than larger ones, leading to a larger stabilization by electrostatic attractive interactions. As a result, more counter charged ions bind to the colloidal particles and colloidal charges are screened more strongly. Secondly, the local density of counter charged ions in contact with colloidal particles increases as the size of the

counter charged ions becomes smaller, leading to a stronger attractive interaction between colloidal particles, arising from the enhanced effects due to the translational motion of counter charged ions. However, these physical factors are not so important once the cation size becomes sufficiently large, and the results for K^+ and Cs^+ are not very different. Here we emphasize that when the colloidal charges are negative, the PMFs in cases of sufficiently high electrolyte solution are considerably more attractive than those shown in figure 1(a).
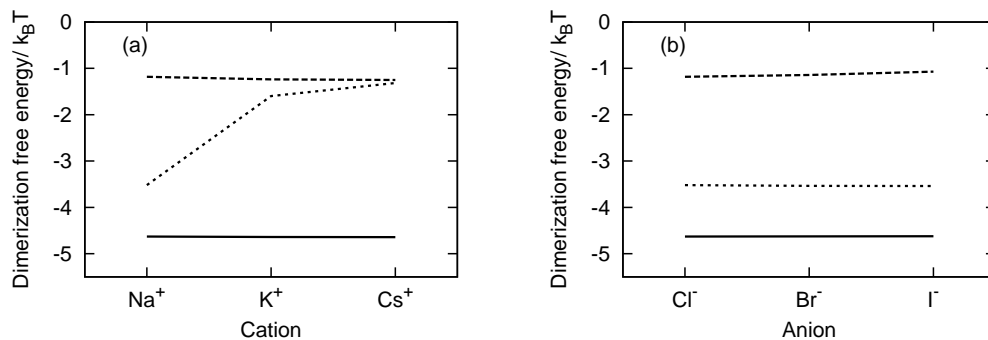
Figure 4. Dimerization free energy between colloidal particles immersed in our model electrolyte solution. The electrolyte concentration is 0.1 M. The total packing fraction of the solution ϕ_t is fixed at 0.383. Solid: $Q_M = 0$, Dash: $Q_M = +5e$, Dots: $Q_M = -5e$. (a) The dependence on cation species (the electrolytes tested are NaCl, KCl, and CsCl). (b) The dependence on anion species (the electrolytes tested are NaCl, NaBr, and NaI).
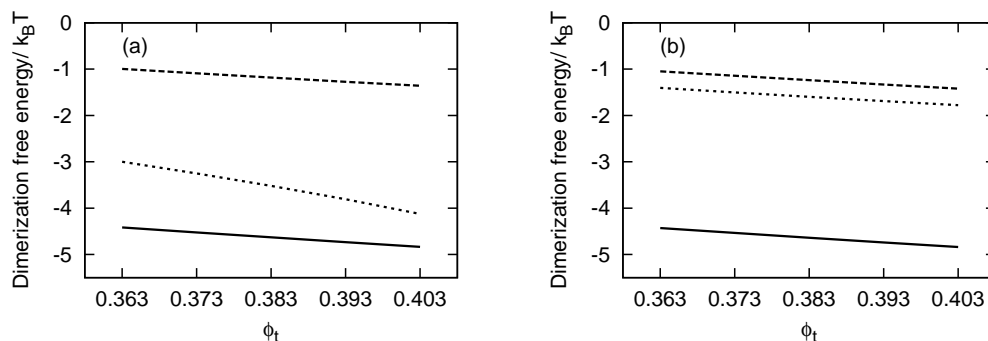

Figure 5. Dimerization free energy between colloidal particles with respect to ϕ_t. The electrolyte concentration is 0.1 M. Solid: $Q_M = 0$, Dash: $Q_M = +5e$, Dots: $Q_M = -5e$. (a) NaCl. (b) KCl.

Next, ϕ_t is varied as the major parameter. The relations between $\Phi_{min}/k_B T$ and ϕ_t observed for NaCl and KCl are illustrated in figure 5(a) and (b), respectively. In all cases $\Phi_{min}/k_B T$ takes a larger negative value as ϕ_t becomes higher. This behavior is expected because the attractive interaction induced by the translational motion of solvent molecules and ions is roughly proportional to the number density of the solution. It is known for real aqueous electrolyte solutions that ϕ_t becomes higher with added electrolytes due to electric striction (i.e., ϕ_t is much higher than 0.383 for any of NaCl, KCl, CsCl, NaBr, and NaI solutions) [31]. Further, as the ionic size becomes smaller, the electric striction becomes stronger and ϕ_t becomes larger. If this effect is taken into consideration, $\Phi_{min}/k_B T$ in figure 4(a) and (b) shifts to more negative values furthermore, this shift being larger for smaller ions.

From the above discussions, we can draw the following conclusions. The contact of uncharged colloidal particles is further stabilized as the electrolyte concentration becomes higher, and the ability of electrolytes to stabilize the contact follows the Hofmeister series for both cations and

anions. The ability of electrolytes to screen the electrostatic repulsion between negatively charged colloidal particles is strongly dependent on cation species and also follows the Hofmeister series. These are consistent with the experimental observations known for the conformational transition of biopolymers with many negatively charged groups and the salting-out phenomenon for neutral proteins. As for the contact of positively charged colloidal particles, however, our result indicates that it is further stabilized as the anion size decreases, which conflicts with the experimental data supporting the inverse Hofmeister series. This contradiction stems from the simplification of the solvent model. In fact, the inverse Hofmeister series was well reproduced by Kinoshita and Harano [17] who employed a more detailed model for water, SPC/E, in which H and O sites carry partial charges. In this model the hydration of ions can be described. Moreover, the strength of the hydration becomes stronger as the ionic size decreases. In the previous paragraph, we mentioned that more counter charged ions tend to bind to the charged colloidal particles as the size of the counter charged ions become smaller (factor 1). However, for the counter charged ions to reach the binding, they should be dehydrated. This dehydration penalty becomes larger as the ionic size decreases (factor 2). The screening ability of counter charged ions is determined by the interplay of the two opposing factors. Kinoshita and Harano showed that factor 1 dominates for cations whereas factor 2 is more important for anions. Our simple model in the present study is not capable of elucidating factor 2.

4. Concluding remarks

This article deals with the interaction (PMF) between like-charged colloidal particles immersed in a simple model of aqueous electrolyte solution using the OZ-HNC theory. The solvent molecules are modeled as neutral hard spheres, and colloidal particles, anions, and cations are taken to be charged hard spheres. Uncharged (neutral) colloidal particles are also considered. The Coulomb potentials between ion-ion, ion-colloidal particle, and colloidal particle-colloidal particle pairs are divided by the dielectric constant of water. This simple model is employed to exclusively address the effects due to solvent granularity (i.e., the translational motion of solvent molecules) and serves as a first-step improvement of the so-called primitive model. The effects of electrolyte concentration and 1-1 electrolyte species (NaCl, KCl, CsCl, NaBr, and NaI) on the interaction between uncharged, positively charged, and negatively charged colloidal particles are analyzed and discussed in detail.

When the electrolyte concentration is sufficiently low, the conventional picture that like-charged colloidal particles interact through the electric double layer is acceptable in the sense that the interaction is always repulsive. When the electrolyte concentration is sufficiently high (e.g., higher than $1 \cdot 10^{-1}$ M), however, regions where the interaction is attractive appear. In particular, the interaction near the contact can be strongly attractive with the stabilization of the dimer of colloidal particles though the direct van der Waals attraction is not incorporated in the model. The attractive interaction in our model is induced by the solvent granularity.

Several authors [5–15] have emphasized the crucial importance of attractive interactions driven by the translational motion of solvent molecules, namely solvent granularity, in biological systems: It plays a crucial role in protein folding, protein aggregation, and in a variety of self-assembling processes. The only force which could predominate over the entropically driven interaction, is the strong electrostatic force between highly charged groups in biomolecules. However, in these cases, the electrolyte concentration is about 0.15 M, which is sufficiently high to screen the electrostatic force. In other words, the electrolytes such as NaCl in biological systems are likely to play a major role in the entropically induced interactions.

The stabilization of contact between uncharged colloidal particles is progressively enhanced as more electrolytes are added to the solution, and this effect becomes stronger as the cation or anion size decreases (result 1). The ability of electrolytes to screen the electrostatic repulsion between negatively charged colloidal particles is strongly dependent on cation species and becomes higher as the cation size decreases (result 2). The ability of electrolytes to screen the electrostatic repulsion between positively charged colloidal particles becomes higher as the anion size decreases while its dependence on anion species is much weaker (result 3). Only result 3 is inconsistent with

the analysis made by Kinoshita and Harano [17] who employed a more detailed model for water, and with the experimental observations known for conformational transition of biopolymers. More counter charged ions tend to bind to the charged colloidal particles as the size of the counter charged ions becomes smaller (factor 1). However, the counter charged ions should be dehydrated to reach the binding. This dehydration penalty becomes larger as the ionic size decreases (factor 2). The ability of counter charged ions to enable stronger binding and screening of the colloidal charges is determined by the interplay of the two opposing factors. Kinoshita and Harano showed that factor 1 dominates for cations whereas factor 2 is more important for anions. Our simple model in the present study is not capable of elucidating factor 2.

Acknowledgements

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Взаємодія між одноіменно зарядженими колоїдними частинками у водних розчинах електролітів: притягальна компонента, що виникає за рахунок дискретності розчинника

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Потенціал середньої сили між одноіменно зарядженими колоїдними частинками, поміщеними у водний розчин електроліту, вивчається методами теорії інтегральних рівнянь. Молекули розчинника моделюються твердими сферами, а іони та колоїдні частинки розглядаються як заряджені тверді сфери. Кулонівські взаємодії між іонами та колоїдними частинками включають діелектричну сталу води. Ця проста модель використана для врахування ефектів дискретності розчинника, якими нехтують в примітивній моделі. Ван дер Ваальсовим притяганням, яке є суттєвою рисою теорії ДЛВО, в даній моделі нехтуються. Тим не менше, притягальні області виникають в потенціалі середньої сили при достатньо високих іонних концентраціях. Зокрема, взаємодія на малих відстанях є достатньо притягальною, щоб стабілізувати колоїдну систему. Ця поведінка виникає за рахунок ефектів трансляційного руху молекул розчинника.

Ключові слова: *колоїдна частинка, розчин електроліту, потенціал середньої сили, теорія інтегральних рівнянь, теорія ДЛВО, дискретність розчинника*

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