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Biophysical Chemistry 57 (1996) 189–203

Biophysical Chemistry

Electrostatic interaction between two charged spherical molecules

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Received 20 October 1994; revised 19 January 1995; accepted 13 March 1995

Abstract

An explicit analytic expression is obtained for the electrostatic energy of the interaction between two ion-impenetrable space-charged hard spheres as a model for spherical molecules in an electrolyte solution on the basis of the linearized Poisson–Boltzmann equation. An explicit expression for the potential distribution in a 3D-space is also found. The polarization effects due to the mutual influence between the spheres are taken into account. The analysis is done by assuming different dielectric permittivities of the respective spheres and of the solution as well. It is shown that the correction terms in the expression for the total energy of interaction arising from the polarization effects always correspond to forces of attraction between the spheres. The contribution of these terms to the total energy of interaction depends on the distance between the two spheres and the dielectric permittivities of the spheres and the solution as well as on the electrolyte concentration in the solution. A numerical simulation of the potential field topography is carried out at several values of the Debye–Hückel parameter. It is shown that the polarization effect can produce significant changes in the potential distribution in the case of strong interacting spheres.

Keywords: Electrostatic interaction; Spherical molecules; Potential distribution

1. Introduction

Electrostatic interactions between charged molecules can be an important factor responsible for the behavior and properties of an ensemble of molecules [1]. This is the reason for which a great number of studies have been provided in order to determine the electrostatic contributions in many aspects such as crystal state stability [2], mechanical properties of the crystal [3] and so on.

For the purpose of describing these interactions it is necessary to make an appropriate model. The most widespread approach is the so called 'spherical molecules' model.

A great number of models exist by now, any of them being applicable to some appropriate real situations.

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SSDI 0301-4622(95)00056-9

Particularly, methods proposed in [4–7] are suitable for describing the electrostatic interactions between spheres in media of a homogeneous dielectric permittivity. A method for calculating the electrostatic interactions is proposed in [8] concerning a charged sphere interaction with a hard plate. This is applicable to the interaction of monolayer membranes with charged spheres.

In models describing electrostatic interactions among large molecules it is of great importance to take into account the nonhomogeneity of the dielectric permittivity. That is why the three-layer model is the closest one to the real conditions [9].

In this work we extend the method described in [6,7], which has been applied originally to the electrostatic interaction of two *surface*-charged hard spheres as a model for the interaction of colloidal particles, to the case of the interaction between two *space*-charged hard spheres as a model for the interaction of charged spherical molecules. We consider the situation in which the interior of each sphere has a dielectric permittivity that may differ from that of the solution.

2. Theory

In this section we will obtain an analytical solution of the problem of interaction between two charged spheres. For this purpose, it is convenient to find a solution in case of non-interacting spheres (the zeroth-order approximation), in case of weakly interacting spheres (the first-order approximation) and finally, to get a solution of the full problem.

2.1. Potential distribution due to two non-interacting spheres (the zeroth-order approximation)

In real situations this means that the spheres are far apart from each other in a surrounding solution of a high electrolyte concentration (i.e., large ionic strength).

Let us consider two non-interacting space-charged hard spheres of radius a_1 and a_2, and relative dielectric permittivities ε_1 and ε_2, respectively, the distance between the sphere centers being R, as shown in Fig. 1, where $H = R - a_1 - a_2$ is the closest distance between their surfaces. The spheres are surrounded by an electrolyte solution of dielectric permittivity ε and N ionic species of valence z_i and bulk concentration (number density) n_i $(i = 1, 2,..., N)$. The Debye–Hückel parameter of the solution is given by $\kappa = \sum_{i=1}^{N} e^2 z_i^2 n_i / \varepsilon\varepsilon_0 k_B T)^{1/2} = (2000 e^2 I N_A / \varepsilon\varepsilon_0 k_B T)^{1/2}$, where e is the elementary electric charge, ε_0 is the permittivity of a vacuum, k_B is the Boltzmann constant, N_A is Avogadro's number, I is the ionic strength of the solution, and T is the absolute temperature. The volume charge density of spheres 1 and 2 are denoted as ρ_1 and ρ_2, respectively.

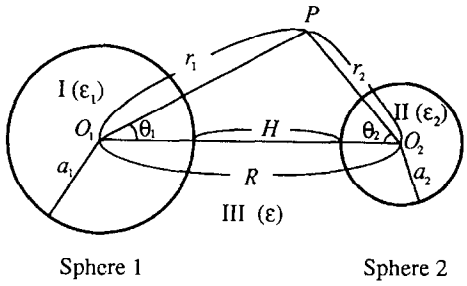


Fig. 1. Schematic representation of the system under consideration.

In order to find the potential distribution it is necessary to separate the space into three regions as follows:
(i) region I occupied by the sphere 1;
(ii) region II occupied by the sphere 2; and
(iii) region III taken by the unlimited solution.

Since we suppose an uniform charge distribution inside the spheres, it is clear that the field will be central–symmetric in the absence of interaction.

Let us choose two coordinate systems (r_1, θ_1, ϕ_1), whose origin coincides with the center of sphere $1(O_1)$, and (r_2, θ_2, ϕ_2) with its origin at the center of the second sphere (O_2). The z-axis for both coordinate systems is directed along the vector O_1O_2. Then we can find the potential created by the sphere 1 by solving the Poisson equation for the region I:

$$\Delta\psi_{\mathrm{in},1} = -\frac{\rho_1}{\varepsilon_1\varepsilon_0}. \tag{1}$$

As a result of symmetry of the system, Eq. (1) can be expressed as follows:

$$\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial\psi_{\mathrm{in},1}(r_1)}{\partial r_1}\right) = -\frac{\rho_1}{\varepsilon_0\varepsilon_1}, \tag{2}$$

which has a solution

$$\psi_{\mathrm{in},1}(r_1) = -\frac{\rho_1 r_1^2}{6\varepsilon_1\varepsilon_0}. \tag{3}$$

In order to obtain the full expression for the solution to Eq. (1), it is necessary to add the general solution of the homogeneous equation for Eq. (1), that is:

$$\psi_{\mathrm{in},1} = \sum_{n=0}^{\infty}\sum_{m=o}^{\infty}\left(A_n r_1^n + \frac{B_n}{r_1^{n+1}}\right)P_n^{|m|}(\cos\theta_1)\mathrm{e}^{i|m|\phi_1}, \tag{4}$$

where $P_n^{|m|}(z)$ are the Legendre polynomials, and A_n and B_n are constants to be determined.

In the case of central symmetry, $n = m = 0$ and B_n must be zero, since the potential must be finite at $r_1 = 0$. Eq. (4) thus reduces to $\psi_{\mathrm{in},1} = A$. Then the solution for the region I is:

$$\psi_{\mathrm{in},1}^{(0)} = -\frac{\rho_1 r_1^2}{6\varepsilon_1\varepsilon_0} + A, \tag{5}$$

where with superscript '(0)' we mark the zeroth-order solution inside sphere 1 (the region I).

In order to find the solution for the region III we have to solve the linearized Poisson–Boltzmann equation

$$\Delta\psi = \kappa^2\psi. \tag{6}$$

Noting the condition that the potential should become zero at $r_1 \to \infty$, the solution to Eq. (6) should be:

$$\psi_1^{(0)} = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} B_n\frac{K_{n+1/2}(r_1)}{\sqrt{r_1}}P_n^{|m|}(\cos\theta_1)\mathrm{e}^{i|m|\phi_1}, \tag{7}$$

where with superscript '(0)' and subscript '1' we mark the potential created by the sphere 1 in the zeroth-order approximation.

As a result of central symmetry, Eq. (7) reduces to

$$\psi_1^{(0)}(r_1) = B_o\frac{\mathrm{e}^{-\kappa r_1}}{r_1}. \tag{8}$$

Eqs. (5) and (8) are the general solutions to Eqs. (1) and (6). In order to obtain the solution of the present problem, it is necessary to apply the boundary conditions on the surface of the sphere 1:

$$\psi_{\mathrm{in},1}(a_1^-,\theta_1) = \psi(a_1^+,\theta_1), \tag{9}$$

$$\varepsilon_1 \frac{\partial \psi_{in,1}}{\partial r_1}\bigg|_{r_1=a_1^-} = \varepsilon \frac{\partial \psi}{\partial r_1}\bigg|_{r_1=a_1^+}. \tag{10}$$

Eq. (10) corresponds to a lack of surface charges on sphere 1.

Let us now apply the boundary conditions given above and after some calculations and we can obtain the following expressions for the potentials $\psi_{\mathrm{in},1}^{(0)}$ and $\psi_1^{(0)}$:

$$\psi_{\mathrm{in},1}^{(0)}(r_1) = \frac{\rho_1 a_1^2[\varepsilon(\kappa a_1 + 1) + 2\varepsilon_1]}{6\varepsilon_1 \varepsilon\varepsilon_0(\kappa a_1 + 1)} - \frac{\rho_1 r_1^2}{6\varepsilon_1 \varepsilon_0} \tag{11}$$

$$\psi_1^{(0)}(r_1) = \frac{\rho_1 a_1^3 e^{\kappa a_1}}{3\varepsilon\varepsilon_0(\kappa a_1 + 1)} \frac{e^{-\kappa r_1}}{r_1} \tag{12}$$

Similarly, by applying the boundary conditions on the surface of sphere 2, viz.,

$$\psi_{\mathrm{in},2}(a_2^-,\theta_2) = \psi(a_2^+,\theta_2), \tag{13}$$

$$\varepsilon_2 \frac{\partial \psi_{\mathrm{in},2}}{\partial r_2}\bigg|_{r_2=a_2^-} = \varepsilon \frac{\partial \psi}{\partial r_2}\bigg|_{r_2=a_2^+}, \tag{14}$$

we can obtain the following expressions of $\psi_{\mathrm{in},2}^{(0)}$ and $\psi_1^{(0)}$ for sphere 2:

$$\psi_{\mathrm{in},2}^{(0)}(r_2) = \frac{\rho_2 a_2^2[\varepsilon(\kappa a_2 + 1) + 2\varepsilon_2]}{6\varepsilon_2 \varepsilon\varepsilon_0(\kappa a_2 + 1)} - \frac{\rho_2 r_2^2}{6\varepsilon_2 \varepsilon_0}, \tag{15}$$

$$\psi_2^{(0)}(r_2) = \frac{\rho_2 a_2^3 e^{\kappa a_2}}{3\varepsilon\varepsilon_0(\kappa a_2 + 1)} \frac{e^{-\kappa r_2}}{r_2}, \tag{16}$$

where $\psi_2^{(0)}$ satisfies the Poisson equation for the region II

$$\Delta\psi_{\mathrm{in},2} = -\frac{\rho_2}{\varepsilon_2 \varepsilon_0}. \tag{17}$$

Thus in the zeroth-order approximation the solution for the region III can be given by a superposition of ψ_1^0 and $\psi_2^{(0)}$, that is:

$$\psi^{(0)} = \psi_1^{(0)} + \psi_2^{(0)} = \frac{\rho_1 a_1^3 e^{\kappa a_1}}{3\varepsilon\varepsilon_0(\kappa a_1 + 1)} \frac{e^{-\kappa r_1}}{r_1} + \frac{\rho_2 a_2^3 e^{\kappa a_2}}{3\varepsilon\varepsilon_0(\kappa a_2 + 1)} \frac{e^{-\kappa r_2}}{r_2}, \tag{18}$$

outside spheres 1 and 2.

In our further consideration we will call this solution the zeroth-order asymptotic solution, because we have not taken into account the interaction between the two spheres. Taking into account this interaction leads to appearance of perturbation terms in the expression for the potentials (11), (15) and (18).

2.2. Potential distribution and energy of interaction between two interacting spheres (the first-order approximation)

Let us consider again the system given in Fig. 1 but taking into account the interaction between the spheres. In this case we cannot suppose a central symmetry of the general solution any more.

We assume the following scheme: The central–symmetrical potential $\psi_1^{(0)}$ created by sphere 1 in the zeroth-order approximation (without taking into account the interaction) polarizes the sphere 2 and induces polarization charges on the surface of the sphere 2. In this way it will break the boundary conditions for sphere 2 (Eqs. (13) and (14)). One thus needs the correction potential terms $\psi_{in,2}^{(1)}$ and $\psi_1^{(1)}$ in order that the boundary conditions (Eqs. (13) and (14)) on sphere 2 become satisfied again. The additional potential term $\psi_1^{(1)}$ in turn polarizes the sphere 1 back and will break the boundary conditions for the sphere 1 (Eqs. (9) and (10)) so that one needs another correction term $\psi_1^{(2)}$. In the first-order approximation, however, we will limit our consideration up to $\psi_{in,2}^{(1)}$ and $\psi_1^{(1)}$ and we will not take into account the further influence of the perturbed potentials on the spheres. This is reasonable since the influence decreases as $e^{\kappa H}$, $e^{-2\kappa H}$, $e^{-3\kappa H}$ and etc. [6,7].

After this introductory explanation, the problem to be solved can be considered as follows:

In the region II, the potential is expressed as

$$\psi_{in,2}^{(0)} + \psi_{in,2}^{(1)}, \tag{19}$$

where $\psi_{in,2}^{(1)}$ arises under the action of the zeroth-order potential $\psi_1^{(0)}$ of sphere 1 on sphere 2. It should be mentioned here that $\psi_{in,2}^{(1)}$, which arises under the action of $\psi_1^{(0)}$, will thus also change the potential outside sphere 2. Then the field outside the sphere 2 is changed from $\psi_1^{(0)} + \psi_2^{(0)}$ into

$$\psi_1^{(0)} + \psi_2^{(0)} + \psi_1^{(1)}, \tag{20}$$

outside sphere 2.

The additional potential $\psi_1^{(1)}$ takes the same form as in Eq. (7) with $m = 0$, since the symmetry along the z-axis still remains in this case. We thus have

$$\psi_1^{(1)}(r_2,\theta_2) = \sum_{n=0}^{\infty} B_n \frac{K_{n+1/2}(\kappa r_2)}{\sqrt{r_2}} P_n(\cos\theta_2), \tag{21}$$

outside sphere 2, where $K_{n+1/2}(z)$ are the modified Bessel functions of the second kind, and $\psi_{in,2}^{(1)}$ takes the form

$$\psi_{in,2^{(1)}}(r_2,\theta_2) = \sum_{n=0}^{\infty} C_n r_2^n P_n(\cos\theta_2), \tag{22}$$

inside sphere 2, where B_n and C_n are constants to be determined so as to satisfy the boundary conditions (13) and (14). It can easily be shown that Eq. (20) (as combined with Eq. (21)) satisfies the linearized Poisson–Boltzmann Eq. (6), while Eq. (19) (with Eq. (22)) is a solution of the Poisson Eq. (17).

In order to further satisfy the boundary conditions on sphere 2 it is necessary to express $\psi_1^{(0)}$ (Eq. (12)) only with the parameters of the second coordinate system. It is possible to use the relation

$$\frac{\exp(-\kappa r_i)}{r_i} = \sum_{n=0}^{\infty} (2n+1) \frac{K_{n+1/2}(\kappa R)}{\sqrt{R}} \frac{I_{n+1/2}(\kappa r_j)}{\sqrt{r_j}} P_n(\cos\theta_j), \ (i,j = 1,2; i \neq j), \tag{23}$$

where $I_{n+1/2}(z)$ are the modified Bessel functions of the first kind (Eq. (23) is correct for $rj < \infty$, because at infinity $I_{n+1/2}(\kappa rj)$ is unlimitedly large). Now we can rewrite Eq. (20) using only the parameters of the second coordinate system:

$$\begin{aligned}
\psi_1^{(0)} + \psi_2^{(0)} + \psi_1^{(1)} &= \frac{\rho_1 a_1^3 e^{\kappa a_1}}{3\varepsilon\varepsilon_0(\kappa a_1 + 1)} \frac{e^{-\kappa r_1}}{r_1} + \frac{\rho_1 a_1^3 e^{\kappa a_2}}{3\varepsilon\varepsilon_0(\kappa a_2 + 1)} \frac{e^{-\kappa r_2}}{r_2} + \psi_1^{(1)} \\
&= \frac{\rho_1 a_1^3 e^{\kappa a_1}}{3\varepsilon\varepsilon_0(\kappa a_1 + 1)} \sum_{n=0}^{\infty} (2n+1) \frac{K_{n+1/2}(\kappa R)}{\sqrt{R}} \frac{I_{n+1/2}(\kappa r_2)}{\sqrt{r_2}} P_n(\cos\theta_2) \\
&\quad + \frac{\rho_2 a_2^3 e^{\kappa a_2}}{3\varepsilon\varepsilon_0(\kappa a_2 + 1)} \frac{e^{-\kappa r_2}}{r_2} + \sum_{n=0}^{\infty} B_n \frac{K_{n+1/2}(\kappa r_2)}{\sqrt{r_2}} P_n(\cos\theta_2),
\end{aligned} \tag{24}$$

outside sphere 2. The functions $\psi_1^{(1)}$ and $\psi_{in,2}^{(1)}$ must be determined so as to satisfy Eqs. (13) and (14),

$$\psi_{in,2^{(1)}}(a_2,\theta_2) = \psi_1^{(0)}(a_2,\theta_2) + \psi_1^{(1)}(a_2,\theta_2), \tag{25}$$

$$\varepsilon_2 \frac{\partial \psi_{in,2}^{(1)}}{\partial r_2}\bigg|_{r_2=a_2^-} - \varepsilon \frac{\partial\left[\psi_1^{(0)} + \psi_1^{(1)}\right]}{\partial r_2}\bigg|_{r_2=a_2^+} = 0, \tag{26}$$

on sphere 2. Thus we find that $\psi_1^{(1)}$ and $\psi_{in,2}^{(1)}$ take the form

$$\psi_1^{(1)}(r_2,\theta_2) = \psi_{o1} a_1 \exp(\kappa a_1) \sum_{n=0}^{\infty} (2n+1) H_n(2) \frac{K_{n+1/2}(\kappa R)}{\sqrt{R}} \times \frac{K_{n+1/2}(\kappa r_2)}{\sqrt{r_2}} P_n(\cos\theta_2), \tag{27}$$

$$\psi_{in,2}^{(1)}(r_2,\theta_2) = \psi_{o1} a_1 \exp(\kappa a_1) \sum_{n=0}^{\infty} (2n+1)\left(\frac{r_2}{a_2}\right)^n \frac{K_{n+1/2}(\kappa R)}{\sqrt{R}} \times \left[\frac{I_{n+1/2}(\kappa a_2)}{\sqrt{a_2}} + H_n(2)\frac{K_{n+1/2}(\kappa a_2)}{\sqrt{a_2}}\right] P_n(\cos\theta_2), \tag{28}$$

where $H_n(i)$ $(i = 1, 2)$ are defined by:

$$H_n(i) = -\frac{I'_{n+1/2}(\kappa a_i) - (1 + 2n\varepsilon_i/\varepsilon) I_{n+1/2}(\kappa a_i)/2\kappa a_i}{K'_{n+1/2}(\kappa a_i) - (1 + 2n\varepsilon_i/\varepsilon) K_{n+1/2}(\kappa a_i)/2\kappa a_i} = \frac{I_{n-1/2}(\kappa a_i) - (n + 1 + n\varepsilon_i/\varepsilon) I_{n+1/2}(\kappa a_i)/\kappa a_i}{K_{n-1/2}(\kappa a_i) + (n + 1 + n\varepsilon_i/\varepsilon) K_{n+1/2}(\kappa a_i)/\kappa a_i}, \tag{29}$$

and ψ_{oi} is the unperturbed surface potential of sphere i $(i = 1, 2)$, given by

$$\psi_{oi} = \frac{\rho_i a_i^2}{3\varepsilon\varepsilon_0(\kappa a_i + 1)}, (i = 1, 2). \tag{30}$$

The same problem arises in the case of the action of $\psi_2^{(0)}$ created by the sphere 2 upon the sphere 1 so that one needs additional terms $\psi_2^{(1)}$ and $\psi_{in,1}^{(1)}$. The same relations can be found for these potentials.

$$\psi_2^{(1)}(r_1\theta_1) = \psi_{o2} a_2 \exp(\kappa a_2) \sum_{n=0}^{\infty} (2n+1) H_n(1) \frac{K_{n+1/2}(\kappa R)}{\sqrt{R}} \times \frac{K_{n+1/2}(\kappa r_1)}{\sqrt{r_1}} P_n(\cos\theta_1), \tag{31}$$

$$\psi_{in,1}^{(1)}(r_1,\theta_1) = \psi_{o2} a_2 \exp(\kappa a_2) \sum_{n=0}^{\infty} (2n+1)\left(\frac{r_1}{a_1}\right)^n \frac{K_{n+1/2}(\kappa R)}{\sqrt{R}} \times \left[\frac{I_{n+1/2}(\kappa a_1)}{\sqrt{a_1}} + H_n(1)\frac{K_{n+1/2}(\kappa a_1)}{\sqrt{a_1}}\right] P_n(\cos\theta_1). \tag{32}$$

Then in the first-order approximation the potential distribution is given by $\psi_{in,1}^{(0)} + \psi_{in,1}^{(1)}$ for the region I, $\psi_{in,2}^{(0)} + \psi_{in,2}^{(1)}$ for the region II and $\psi^{(1)} = \psi_1^{(0)} + \psi_2^{(1)} + \psi_1^{(1)} + \psi_2^{(1)}$ for the region III.

2.3. Interaction between two spheres — exact analytical solution

Continuing the procedure described in previous subsections, the full solution can be obtained in the following way.

The potential $\psi_1^{(0)}$ created by the sphere 1 without taking into account interaction between spheres (the

zeroth-order approximation) breaks the boundary conditions on the surface of the sphere 2 (Eqs. (13) and (14)), which have already been satisfied by the unperturbed potential $\psi_2^{(0)}$ of the sphere 2 in the zeroth-order approximation. This potential $\psi_1^{(0)}$ induces surface charges on the surface of sphere 2. Then the induced surface charges produce additional (perturbation) terms ($\psi_1^{(1)}$ and $\psi_{\mathrm{in},2}^{(1)}$), which have been derived in the first-order approximation (Eqs. (27) and (28)). Satisfying the boundary conditions on the surface of the sphere 1, we can obtain expressions for undefined constants appearing in the perturbation terms [6,7].

Then the potential $\psi_1^{(1)}$ in turn reaches the surface of the sphere 1 and also breaks the boundary conditions on the sphere 1 (Eqs. (9) and (10)), which have already been satisfied by the unperturbed potential $\psi_1^{(0)}$ of the sphere 2. It induced surface charges on the surface of the sphere 1, and these surface charges generate new perturbation terms — $\psi_1^{(2)}$ and $\psi_{\mathrm{in},1}^{(2)}$. These new terms can be found by applying the boundary conditions on the sphere 1. In this way we may assume that the full expression for the potential function has a following form:

$$\Psi(r_1,\theta_1) = \Psi_1^{(0)} + \Psi_2^{(0)} + \left[\Psi_1^{(1)} + \Psi_1^{(2)} + \Psi_1^{(3)} + \ldots\right] + \left[\Psi_2^{(1)} + \Psi_2^{(2)} + \Psi_2^{(3)} + \ldots\right]$$

$$= \sum_{k=0}^{\infty} \Psi_1^{(k)} + \sum_{k=0}^{\infty} \Psi_2^{(k)}, \tag{33}$$

outside spheres 1 and 2,

$$\psi_{\mathrm{in},1}(r_1,\theta_1) = \psi_{\mathrm{in},1}^{(0)} + \psi_{\mathrm{in},1}^{(1)} + \psi_{\mathrm{in},1}^{(2)} + \psi_{\mathrm{in},1}^{(3)} + \ldots = \sum_{k=0}^{\infty} \psi_{\mathrm{in},1}^{(k)}, \tag{34}$$

inside sphere 1,

$$\psi_{\mathrm{in},2}(r_2,\theta_2) = \psi_{\mathrm{in},2}^{(0)} + \psi_{\mathrm{in},2}^{(1)} + \psi_{\mathrm{in},2}^{(2)} + \psi_{\mathrm{in},2}^{(3)} + \ldots = \sum_{k=0}^{\infty} \psi_{\mathrm{in},2}^{(k)}, \tag{35}$$

inside sphere 2.

Repeating the same procedure on the sphere 2 and after that again on the sphere 1 and etc., we can find the following perturbation terms arising from the mutual electrostatic interaction between the spheres 1 and 2 ($\nu = 1, 2, \ldots$):

$$\psi_1^{(2\nu-1)}(r_1,\theta_1) = \psi_{o1} a_1 \exp(\kappa a_1) \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \ldots \sum_{n_{2\nu-1}=0}^{\infty} M_{21}(n_1,n_2,\ldots,n_{2\nu-1})$$

$$\times \frac{K_{n_1+1/2}(\kappa R)}{\sqrt{R}} \frac{K_{n_{2\nu-1}+1/2}(\kappa r_2)}{\sqrt{r_2}} P_{n_{2\nu-1}}(\cos\theta_2),$$

$$= \psi_{o1} a_1 \exp(\kappa a_1) \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \ldots \sum_{n_{2\nu-1}=0}^{\infty} \sum_{n_{2\nu}=0}^{\infty} M_{21}(n_1,n_2,\ldots,n_{2\nu-1})$$

$$\times (2n_{2\nu}+1) B_{n_{2\nu-1}n_{2\nu}} \frac{K_{n_1+1/2}(\kappa R)}{\sqrt{R}} \frac{I_{n_{2\nu}+1/2}(\kappa r_1)}{\sqrt{r_1}} P_{n_{2\nu}}(\cos\theta_1), \tag{36}$$

$$\psi_1^{(2\nu)}(r_1,\theta_1) = \psi_{o1} a_1 \exp(\kappa a_1) \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \ldots \sum_{n_{2\nu}=0}^{\infty} M_{21}(n_1,n_2 \ldots n_{2\nu})$$

$$\times \frac{K_{n_1+1/2}(\kappa R)}{\sqrt{R}} \frac{K_{n_{2\nu}+1/2}(\kappa r_1)}{\sqrt{r_1}} P_{n_{2\nu}}(\cos\theta_1), \tag{37}$$

$$\psi_{\mathrm{in},1}^{(2\nu)}(r_1,\theta_1) = \psi_{o1}a_1\exp(\kappa a_1)\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_{2\nu}=0}^{\infty}\left(\frac{r_1}{a_1}\right)^{n_{2\nu}}\frac{K_{n_1+1/2}(\kappa R)}{\sqrt{R}}$$

$$\times\left[M_{21}(n_1,n_2,\ldots,n_{2\nu-1})B_{n_{2\nu-1}n_{2\nu}}(2n_{2\nu}+1)\frac{I_{n_{2\nu}+1/2}(\kappa a_1)}{\sqrt{a_1}}\right.$$

$$\left.+M_{21}(n_1,n_2,\ldots,n_{2\nu})\frac{K_{n_{2\nu}+1/2}(\kappa a_1)}{\sqrt{a_1}}\right]P_{n_{2\nu}}(\cos\theta_1), \tag{38}$$

$$\psi_{\mathrm{in},2}^{(2\nu-1)}(r_2,\theta_2) = \psi_{o1}a_1\exp(\kappa a_1)\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_{2\nu-1}=0}\left(\frac{r_2}{a_2}\right)^{n_{2\nu-1}}\frac{K_{n_1+1/2}(\kappa R)}{\sqrt{R}}$$

$$\times\left[M_{21}(n_1,n_2,\ldots,n_{2\nu-2})B_{n_{2\nu-2}n_{2\nu-1}}(2n_{2\nu-1}+1)\frac{I_{n_{2\nu-1}+1/2}(\kappa a_2)}{\sqrt{a_2}}\right.$$

$$\left.+M_{21}(n_1,n_2,\ldots,n_{2\nu-1})\frac{K_{n_{2\nu-1}+1/2}(\kappa a_2)}{\sqrt{a_2}}\right]P_{n_{2\nu-1}}(\cos\theta_2), \tag{39}$$

with

$$M_{21}(n_1,n_2,\ldots,n_{2\nu}) = (2n_1+1)(2n_2+1)\times\ldots\times(2n_{2\nu}+1)B_{n_1n_2}B_{n_2n_3}\times\ldots\times B_{n_{2\nu-1}n_{2\nu}}$$

$$\times H_{n_1}(2)H_{n_2}(1)\times\ldots\times H_{n_{2\nu-1}}(2)H_{n_{2\nu}}(1),\ (\nu=1,2,\ldots), \tag{40}$$

$$M_{21}(n_1) = (2n_1+1)H_{n_1+1/2}(2), \tag{41}$$

and

$$M_{21}(n_1,n_2,\ldots,n_{2\nu-1}) = (2n_1+1)(2n_2+1)\times\ldots\times(2n_{2\nu-1}+1)\times B_{n_1n_2}B_{n_2n_3}$$

$$\times\ldots\times B_{n_{2\nu-2}n_{2\nu-1}}H_{n_1}(2)H_{n_2}(1)\times\ldots\times H_{n_{2\nu-1}}(2)$$

$$= M_{21}(n_1,n_2,\ldots,n_{2\nu-2})(2n_{2\nu-1}+1)B_{n_{2\nu-2}n_{2\nu-1}}H_{n_{2\nu-1}}(2)$$

$$= M_{21}(n_1,n_2,\ldots,n_{2\nu-2})B_{n_{2\nu-2}n_{2\nu-1}}M_{n_{2\nu-1}}(n_{2\nu-1}),\ (\nu=2,3,\ldots), \tag{42}$$

$$B_{nm} = \sum_{r=0}^{\min\{n,m\}}A_{nmr}\sqrt{\frac{\pi}{2\kappa R}}\,K_{n+m-2r+1/2}(\kappa R), \tag{43}$$

$$A_{nmr} = \frac{\Gamma(n-r+1/2)\Gamma(m-r+1/2)\Gamma(r+1/2)(n+m-r)!(n+m-2r+1/2)}{\pi\Gamma(m+n-r+3/2)(n-r)!(m-r)!r!}, \tag{44}$$

where $\Gamma(z)$ is the gamma function. Note that $\psi_1^{(2\nu)}$ and $\psi_{\mathrm{in},1}^{(2\nu)}$ $(\nu=1,2,\cdots)$ can be interpreted as the 'image' potentials of $\psi_1^{(2\nu-1)}$ with respect to the sphere 1, while $\psi_1^{(2\nu-1)}$ and $\psi_{\mathrm{in},2}^{(2\nu-1)}$ $(\nu=1,2,\cdots)$ as the 'image' potentials of $\psi_1^{(2\nu-2)}$ with respect to the sphere 2.

The corresponding expressions for $\psi_2^{(2\nu-1)}$, $\psi_2^{(2\nu)}$, and $\psi_{\mathrm{in},1}^{(2\nu-1)}$, and $\psi_{\mathrm{in},2}^{(2\nu)}$ $(\nu=1,2,\cdots)$ can be obtained by

the proper interchange $a_1 \leftrightarrow a_2$, $\varepsilon_1 \leftrightarrow \varepsilon_2$, and $\psi_{01} \leftrightarrow \psi_{02}$, in Eqs. (36)–(39). The expressions thus obtained for $\psi_1^{(k)}$, $\psi_2^{(k)}$, $\psi_{\mathrm{in},1}^{(k)}$, and $\psi_{\mathrm{in},2}^{(k)}$ satisfy

$$\sum_{k=0}^{\infty} \psi_{\mathrm{in},i}^{(k)}(a_i,\theta_i) = \sum_{k=0}^{\infty} \left[\psi_i^{(k)}(a_i,\theta_i) + \psi_j^{(k)}(a_i,\theta_i)\right], \tag{45}$$

$$\varepsilon_i \sum_{k=0}^{\infty} \frac{\partial \psi_{\mathrm{in},i}^{(k)}}{\partial r_i}\bigg|_{r_i=a_i^-} - \varepsilon \sum_{k=0}^{\infty} \frac{\partial}{\partial r_i}\left[\psi_i^{(k)} + \psi_j^{(k)}\right]\bigg|_{r_i=a_i^+} = 0, \ (i = 1,2), \tag{46}$$

so that the boundary conditions on the spheres 1 and 2 (Eqs. (9), (10), (13) and (14)) are satisfied.

2.4. Potential energy of electrostatic interaction

The electrostatic interaction energy can be expressed as the free energy of the system consisting of the two spheres 1 and 2 at separation R minus that at infinite separation, viz.,

$$V(R) = F(R) - F(\infty). \tag{47}$$

The free energy of the present system can be obtained by applying a method of Verwey and Overbeek [10]. In the present case the free energy is the sum of the integral of the product $\rho_1\psi_{\mathrm{in},1}/2$ over the volume V_1 of the sphere 1 and that of the product $\rho_2\psi_{\mathrm{in},2}/2$ over the volume V_2 of the sphere 2, viz.,

$$F(R) = +\frac{1}{2}\rho_1 \int_{V_1} \psi_{\mathrm{in},1}(r_1,\theta_1)\mathrm{d}V_1 + \frac{1}{2}\rho_2 \int_{V_2} \psi_{\mathrm{in},2}(r_2,\theta_2)\mathrm{d}V_2, \tag{48}$$

where $\mathrm{d}V_i = 2\pi r_i^2 \sin\theta_i \mathrm{d}r_i \mathrm{d}\theta_i$ $(i = 1, 2)$. Note that Eq. (48) is consistent with the linearized Poisson–Boltzmann Eq. (6). The plus sign of each term on the right side of Eq. (48) corresponds to the situation in which the space charge densities of spheres 1 and 2 (ρ_1 and ρ_2) remain constant during interaction. Eq.(48) together with Eqs. (34), (35) then becomes:

$$V(R) = \sum_{k=1}^{\infty} \left[\frac{1}{2}\rho_1 \int_{V_1} \psi_{\mathrm{in},1}^{(k)}(a_1,\theta_1)\mathrm{d}V_1 + \frac{1}{2}\rho_2 \int_{V_2} \psi_{\mathrm{in},2}^{(k)}(r_2,\theta_2)\mathrm{d}V_2\right], \tag{49}$$

where the internal fields $\psi_{\mathrm{in},1}^{(k)}$, and $\psi_{\mathrm{in},2}^{(k)}$ inside the spheres are related to the external field $\psi_1^{(k)}$, and $\psi_2^{(k)}$ in the solution phase (the region III) by:

$$\psi_{\mathrm{in},1}^{(2\nu-1)}(a_1,\theta_1) = \psi_2^{(2\nu-2)}(a_1,\theta_1) + \psi_2^{(2\nu-1)}(a_1,\theta_1), \quad (\nu = 1,2,\cdots), \tag{50}$$

$$\psi_{\mathrm{in},1}^{(2\nu)}(a_1,\theta_1) = \psi_1^{(2\nu-1)}(a_1,\theta_1) + \psi_1^{(2\nu)}(a_1,\theta_1), \quad (\nu = 1,2,\cdots), \tag{51}$$

$$\psi_{\mathrm{in},2}^{(2\nu-1)}(a_2,\theta_2) = \psi_1^{(2\nu-2)}(a_2,\theta_2) + \psi_1^{(2\nu-1)}(a_2,\theta_2), \quad (\nu = 1,2,\cdots), \tag{52}$$

$$\psi_{\mathrm{in},2}^{(2\nu)}(a_2,\theta_2) = \psi_2^{(2\nu-1)}(a_2,\theta_2) + \psi_2^{2\nu}(a_2,\theta_2), \quad (\nu = 1,2,\cdots). \tag{53}$$

Note that the first term with $k = 0$ in Eq. (49), giving the self energy $F(\infty)$; viz.,

$$F(\infty) = \frac{1}{2}\rho_1 \int_{V_1} \psi_{\mathrm{in},1}^{(0)}\mathrm{d}V_1 + \frac{1}{2}\rho_2 \int_{V_2} \psi_{\mathrm{in},2}^{(0)}\mathrm{d}V_2 \tag{54}$$

does not contribute to the interaction energy $V(R)$, since this term is independent of R. Carrying out the integration after substitution of the expressions for $\psi_{\mathrm{in},1}^{(2\nu)}$ (Eq. (38)) and $\psi_{\mathrm{in},2}^{(2\nu-1)}$ (Eq. (39)) and the corresponding expressions for $\psi_{\mathrm{in},1}^{(2\nu-1)}$ and $\psi_{\mathrm{in},2}^{(2\nu)}$, which are obtained by the proper interchange $a_1 \leftrightarrow a_2$,

$\varepsilon_1 \leftrightarrow \varepsilon_2$ and $\psi_{o1} \leftrightarrow \psi_{o2}$ in Eqs. (38) and (39), we obtain the required result for the interaction energy between spheres 1 and 2, viz.,

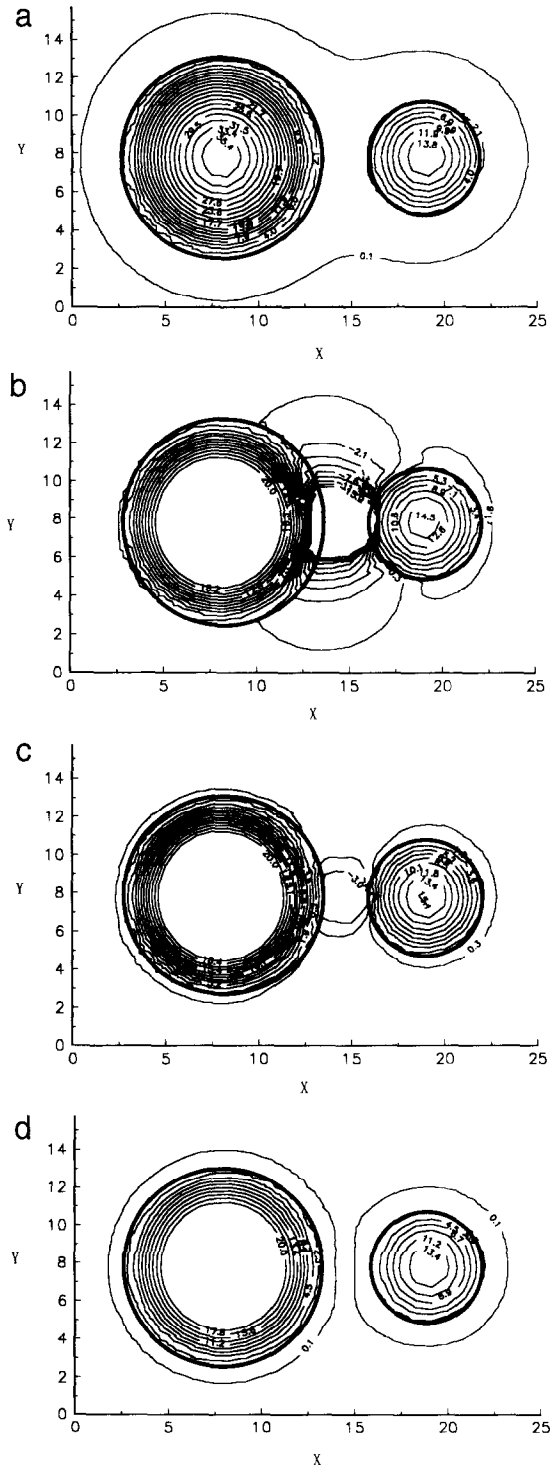
$$
\begin{aligned}
V(R) &= 4\pi\varepsilon\varepsilon_0\psi_{o1}\psi_{o2}a_1a_2\frac{\exp[-\kappa(R-a_1-a_2)]}{R} \\
&+ 2\pi\varepsilon\varepsilon_0\psi_{o1}^2a_1^2\frac{\exp(2\kappa a_1)}{R}\sum_{n=0}^{\infty}(2n+1)H_n(2)K_{n+1/2}^2(\kappa R) \\
&+ 2\pi\varepsilon\varepsilon_0\psi_{o2}^2a_2^2\frac{\exp(2\kappa a_2)}{R}\sum_{n=0}^{\infty}(2n+1)H_n(1)K_{n+1/2}^2(\kappa R) \\
&+ 4\pi\varepsilon\varepsilon_0\psi_{o1}\psi_{o2}a_1a_2\frac{\exp[\kappa(a_1+a_2)]}{R}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}(2n+1)(2m+1)B_{nm} \\
&\times H_n(2)H_m(1)K_{n+1/2}(\kappa R)K_{m+1/2}(\kappa R) + \ldots \\
&+ 2\pi\varepsilon\varepsilon_0\psi_{o1}\psi_{o2}a_1a_2\frac{\exp[\kappa(a_1+a_2)]}{R} \\
&\times \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_{2\nu}=0}[M_{12}(n_1,n_2\ldots n_{2\nu})+M_{21}(n_1,n_2\ldots n_{2\nu})] \\
&\times K_{n_1+1/2}(\kappa R)K_{n_{2\nu}+1/2}(\kappa R) \\
&+ 2\pi\varepsilon\varepsilon_0\sum_{n_1=0}^{\infty}\cdots\sum_{n_{2\nu-1}=0}(2n_{2\nu-1}+1)B_{n_{2\nu-2}n_{2\nu-1}} \\
&\times\left[\psi_{o1}^2a_1^2\frac{\exp(2\kappa a_1)}{R}M_{21}(n_1,n_2\ldots n_{2\nu-2})H_{n_{2\nu-1}}(2)\right. \\
&\left.+\psi_{o2}^2a_2^2\frac{\exp(2\kappa a_2)}{R}M_{12}(n_1,n_2\ldots n_{2\nu-2})H_{n_{2\nu-1}}(1)\right] \\
&\times K_{n_1+1/2}(\kappa R)K_{n_{2\nu-2}+1/2}(\kappa R) + \ldots,
\end{aligned}
\tag{55}
$$

where $H_n(i)$ $(i = 1, 2)$ and $M_{21}(n_1, n_2, \cdots, n_{2\nu})$ are given by Eqs. (29) and (40), and $M_{12}(n_1, n_2, \cdots, n_{2\nu})$ is defined by

$$
\begin{aligned}
M_{12}(n_1,n_2,\cdots,n_{2\nu}) &= (2n_1+1)(2n_2+1)\times\cdots\times(2n_{2\nu}+1)B_{n_1n_2}B_{n_2n_3}\times\cdots\times B_{n_{2\nu-1}n_{2\nu}} \\
&\times H_{n_1}(1)H_{n_2}(2)\times\cdots\times H_{n_{2\nu-1}}(1)H_{n_{2\nu}}(2), \quad (\nu=1,2,\cdots),
\end{aligned}
\tag{56}
$$

which is obtained by the interchange $a_1 \leftrightarrow a_2$ and $\varepsilon_1 \leftrightarrow \varepsilon_2$ in the expression for M_{21} $(n_1, n_2, \cdots, n_{2\nu})$ (Eq. 40), and ρ_1 and ρ_2 are, respectively, expressed in terms of ψ_{o1} and ψ_{o2} (Eq. (30)).

Fig. 2. Potential topography plot in the case of two spheres with radii $a_1 = 5$ Å and $a_2 = 3$ Å, dielectric constants $\varepsilon_1 = 2$ and $\varepsilon_2 = 4$, total charges $q_1 = 6e$ and $q_2 = 3e$, respectively. The spheres are immersed in an unlimited solution with a relative dielectric permittivity of 80 and they are separated at distance $R = 11$ Å. The potential is expressed in $\times 10$ V and calculated for the case of (a) non-interacting spheres at $\kappa = 0.3$ Å^{-1}, (b) interacting spheres at $\kappa = 0.3$ Å^{-1}, (c) interacting spheres at $\kappa = 0.6$ Å^{-1}, (d) interacting spheres at $\kappa = 0.9$ Å^{-1}.


a
b
c
d
X
Y
0
5
10
15
20
25
2
4
6
8
12
14
0.1

3. Discussion

The equation obtained for the potential distribution has been used for numerical simulation of the electrostatic interaction between two spheres. Calculations have been performed at several values of the Debye–Hückel parameter for two values of the relative dielectric permittivity ε of the solution phase (region III).

The topography of the potential produced by two non-interacting spheres is given in Fig. 2a. As can be seen the isopotential curves are concentric with respect to the sphere centers. The potential reaches its maximal value in the core of each sphere, decreasing strongly in the solution phase. We should mention here that some of the curves have a quite rough shape due to the limited number of points for which we have calculated the potential.

The topography of the electrostatic potential in the case of two interacting spheres is shown in Fig. 2b. Comparing the last two figures mentioned above one can see the perturbation of the potential due to the mutual influence between the spheres. The effect of polarization reaches its maximal value between the spheres. The positive potential produced by each sphere induces negative charges on the surface of the other one. As a result, the negative potential created by the induced negative charge perturbs the total electrostatic field. The mutual influence decreases exponentially with increasing distance between the source and the target. This is the reason for which this effect is the strongest on the neighbors surfaces of the spheres.

In the calculation above we have restricted ourselves to the multiple expansion up to $n = 10$. The reason for this is a computing limitation. But as shown by our calculations this does not produce a significant error because the magnitude of the high-order terms (with respect to n) decreases very fast.

With an increasing Debye–Hückel parameter κ (Fig. 2c), the effect of polarization decreases. The potential field deformation is very weak being concentrated on the narrow region between the spheres. This is due to the fact that the screening effect increases twice in this case.

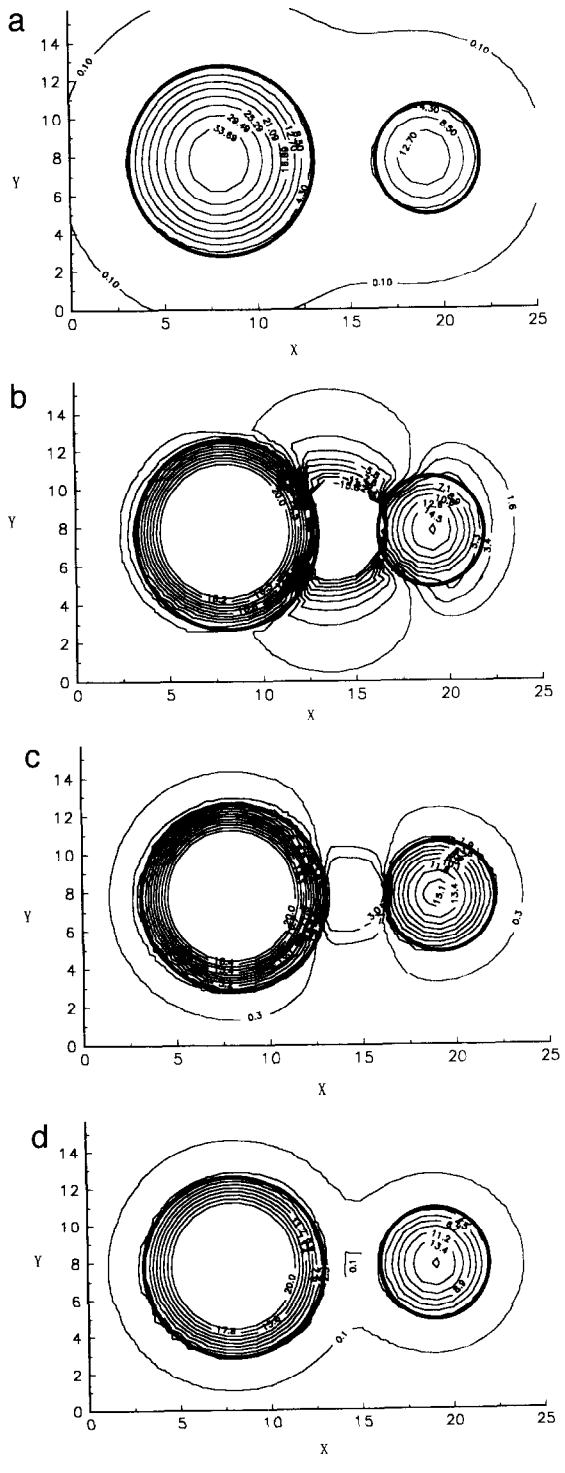
The effect of polarization cannot be observed practically in Fig. 2d. The potential distribution is very similar to that produced by two non-interacting spheres. This is due to the large 'κ' value used during the calculation in this case. The screening effect of the electrolyte ions in the solution phase on the electrostatic potential is so large that the potential on the surface of the target sphere is very low, since the induced surface density can be neglected.

The same numerical simulations have been carried out in the case of the solution dielectric constant being twice smaller. Fig. 3a shows the potential topography in the case of two non-interacting spheres. As a result of decreasing the dielectric constant of the solution, the potential attenuation in the solution is a little slower than in the case of Fig. 2a.

The potential topography of two interacting spheres is presented in Fig. 3b. In this case the mutual influence increases slightly with respect to Fig. 2b. It is due to the smaller value of the dielectric constant of the solution we have used. It should be mentioned here that we gave the Debye–Hückel parameter the same value as in Fig. 2b while we changed the relative dielectric permittivity of the solution. In fact, this means that we increase the ionic strength twice. In this point of view it can be concluded that the effect of polarization can be regulated by varying the dielectric constant and the ionic strength of the solution and the effect of each one of these parameters can compensate each other.

Further increasing of κ produces an additional screening effect of the electrostatic field. As can be seen in Fig. 3c, the magnitude of the induced field decreases significantly. The perturbations are still observable being slightly bigger than in Fig. 2c.

Fig. 3. Potential topography plot in the case of two spheres with radii $a_1 = 5$ Å and $a_2 = 3$ Å, dielectric constants $\varepsilon_1 = 2$ and $\varepsilon_2 = 4$, total charges $q_1 = 6e$ and $q_2 = 3e$, respectively. The spheres are immersed in an unlimited solution with a relative dielectric permittivity of 40 and they are separated at distance $R = 11$ Å. The potential is expressed in $\times 10$ V and calculated for the case of (a) non-interacting spheres at $\kappa = 0.3$ Å^{-1}, (b) interacting spheres at $\kappa = 0.3$ Å^{-1}, (c) interacting spheres at $\kappa = 0.6$ Å^{-1}, (d) interacting spheres at $\kappa = 0.9$ Å^{-1}.


a
b
c
d
X
Y
0
5
10
15
20
25
0
2
4
6
8
10
12
14

The potential distribution in Fig. 3d is quite similar to this in Fig. 3a corresponding to non-interacting spheres. The screening effect produced by the electrolyte ions does not permit a mutual influence between the spheres.

The numerical simulation we have carried out shows that the effect of polarization can produce a significant perturbation in the electrostatic potential topography. In the case of a relatively small Debye–Hückel parameter (see Fig. 2b and Fig. 3b) the charge on the closest surfaces between the spheres are fully perturbed. A relatively strong field having the opposite sign arises in the space between the spheres. As is well known the polarization field always corresponds to forces of attraction. These effects can change dramatically the behavior of a system of interacting charged particles.

In this section we have presented results of our numerical simulations of electrostatic potential topography in case of relatively large κH values. We did not carry out calculations at a small κH, because one of the purposes of the method described above is to find a solution for the problem of two interacting spheres in case when the potential amplitude attenuates in the solution. In the opposite case of simplest dielectric media, i.e., $\kappa = 0$, one can easily find a solution without using the method of 'image' potentials. In our calculations this corresponds to the case of $\kappa H \ll 1$, when $\exp(-\kappa H) \rightarrow 1$. Therefore, this case cannot present the advantages of our method and consequently we did not examine it.

The expressions for the potential distribution and the interaction energy for the system of two *space*-charged spheres are formally the same as those for the case of two interacting *surface*-charged colloidal particles carrying constant surface charge density (7) except for the expressions (Eq. (30) for the unperturbed surface potentials ψ_{oi} of the sphere i ($i = 1, 2$)). In the present paper ψ_{oi} is related to the space charge density ρ_i of the sphere i, while it is related to the surface charge density σ_i.

In order to make this clear, we consider finally the general case where the space charge density ρ_i of the sphere i ($i = 1, 2$) is not a constant but a spherically symmetrical function of r_i. In this case the unperturbed potential distributions outside and inside the sphere i ($i = 1, 2$), $\psi_i^{(0)}(r_i)$ and $\psi_{in,i}^{(0)}(r_i)$, are given by

$$\psi_i^{(0)}(r_i) = \psi_{oi}\frac{a_i}{r_i}\exp[-\kappa(r_i - a_i)], \tag{57}$$

outside sphere i,

$$\psi_{in,i}^{(0)}(r_i) = \frac{1}{\varepsilon\varepsilon_0(1+\kappa a_i)a_i}\int_0^{a_i} r^2\rho_i(r)\mathrm{d}r + \frac{1}{\varepsilon\varepsilon_0}\int_0^{a_i}\left(r - \frac{r^2}{a_i}\right)\rho_i(r)\mathrm{d}r - \frac{1}{\varepsilon\varepsilon_0}\int_0^{r_i}\left(r - \frac{r^2}{r_i}\right)\rho_i(r)\mathrm{d}r, \tag{58}$$

inside sphere i, where ψ_{oi} is the unperturbed surface potential of sphere i ($i = 1, 2$), given by

$$\psi_{oi} = \frac{1}{\varepsilon\varepsilon_0(1+\kappa a_i)a_i}\int_0^{a_i} r^2\rho_i(r)\mathrm{d}r. \tag{59}$$

If the spheres are uniformly charged, i.e., $\rho_i(r_i) = \rho_i$, then the above results reduce those obtained in the present paper, while the particle-fixed charges are located only at the sphere surface, i.e.,

$$\rho_i(r_i) = \sigma_i\delta(r_i - a_i), \tag{60}$$

$\delta(r_i - a_i)$ being Dirac's delta function, then we obtain

$$\psi_{oi}(r_i) = \frac{\sigma_i a_i}{\varepsilon\varepsilon_0(1+\kappa a_i)}, \tag{61}$$

a result for the relationship between the surface charge density and the surface potential of a surface-charged sphere (7).

Acknowledgements

E.A. thanks Dr. T. Ueki for accepting him as a guest scientist and the JISTEC for the STA Fellowship.

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