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Electrostatic repulsion between particles in cement suspensions: Domain of validity of linearized Poisson–Boltzmann equation for nonideal electrolytes

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Abstract

To understand the dispersion of cement particles by superplasticizers, proper quantification of the possible mechanisms involved (electrostatic, steric, and depletion forces) is required. This is an important objective to help understand the origin of unexpected incompatibilities between some cement and superplasticizer combinations and more generally predict the rheological behavior. The relative importance of the electrostatic interaction with respect to steric hindrance is currently under much debate. The debate centered on this topic has not fully explored how the nonideal electrolyte found in cement suspensions effects the simplified Debye–Hückel approximation for evaluation of electrostatic repulsion. In this article, the nonideality of the cement aqueous phase—suspension electrolyte—has been taken into account based on solubility equilibria of the possible ionic species present in typical cement suspensions. By replacing the normally assumed symmetric electrolyte (1:1, 2:2, or 3:3) with a noninteger symmetric electrolyte, the simple Debye–Hückel approach has been shown to remain valid for negative potentials down to around 30 mV. Significant deviations are found for positive potentials greater than 10 mV.

Keywords: Dispersion; Rheology; Workability; Cement; Concrete

1. Introduction

Placing of concrete requires much more water than the cement needs for its hydration. This results in a certain porosity in the hardened concrete lowering its potential mechanical properties and facilitates degradation of this material. By adding small amounts of polymeric admixtures, called superplasticizers, one can greatly decrease the amount of water required to obtain the desired workability and consequently, the porosity, which improves durability. It is recognized that the origin of the effect, which superplasticizers have in concrete, comes from decreasing the attractive forces between cement particles. The effective volume of agglomerates and thereby the effective volume of solids in the suspension is decreased, which improves workability. Getting a reliable estimate of each interparticle force in cement suspensions is an essential step, albeit complicated, to help understand the reasons behind unexpected incompatibilities sometimes encountered between certain cements and superplasticizers. It will help distinguish situations in which unusual chemical effects are induced by the presence of superplasticizers from situations in which abnormal dispersion effects are induced by the cement. Reaching such an ultimate goal will help solve many application-related problems. In the current article, we aim to take into account at least one aspect of the complex interactions between cement particles—the nonideality of the aqueous phase. Many other aspects of this complex system, i.e., nonspherical particles, possible changes in aqueous and solid phase composition as the cement hydrates are beyond the scope of this article and remain for future development.

Until recently, all superplasticizers were highly ionic polymers, usually sodium salts of a polysulfonic or polycarboxylic acids, or both. The mechanisms through which these polymers disperse cement agglomerates were generally attributed to electrostatic repulsion. This was supported by the observation that these polymers adsorbed onto

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cement particles, inducing a substantial increase in the magnitude of the electrostatic potential [1]. However, calculated interparticle potentials indicate that due to the high concentration of electrolytes in the aqueous phase (up to 1 M), the magnitude of the repulsive electrostatic force is never capable of overcoming that of the attractive van der Waals forces. For this reason, it was suggested that steric hindrance of the adsorbed layer had to be the main contribution in dispersion [2–4]. Consequently, more recently, polymers have been introduced that have an adsorbing backbone containing ionic groups on which are grafted side chains of ethylene oxide, designed to stretch out into the solution to enhance the contribution of the steric hindrance [2,4].

The expression for electrostatic repulsion between charged particles is derived from the knowledge of the ion distribution as a function of distance from the charged interface and the way the distribution is disturbed once charged surfaces approach one another. We treat this derivation in greater detail and highlight the introduction of thermodynamics of real solutions for the aqueous phase of cements. Most treatments of electrostatic repulsion are derived at ionic concentrations where the electrolyte behavior can be deemed “ideal” (e.g., $<10^{-3}$ M) and assume the electrolyte to be symmetric. For cements suspensions the electrolyte is a complex concentrated electrolyte (up to 1 M) of variable valence, which cannot be described as an “ideal” solution.

The objective of this article is to present a closer examination of the underlying calculations of the magnitude of the electrostatic repulsion and present a treatment more relevant to cement suspensions. It takes into account the nonideality of the thermodynamics of the aqueous phase of the cement suspension and leads to a modified Poisson–Boltzman-type approach. However, it remains limited by the continuum mean field framework in which such approaches are anchored. The limitations of mean field theory are particularly apparent on close approach (~ 2–5 nm). Finite size effects of the ions are perhaps the most immediate to come to mind. However, important deviations from continuum theory only appear important for polyvalent ions [5], and these essentially result from ion correlation effects. Bearing in mind these possible limitations at very close approach, the article describes an approach using solution data for a specific cement at a given time. It compares interaction potentials for spherical particles as obtained from the usual Poisson–Boltzmann equation using the Debye–Hückel theory for simple symmetric electrolytes combined with a new approach using a noninteger representation of the cement suspension electrolyte.

2. Theory

A brief but complete treatment of the theoretical approach to electrostatic repulsion is presented to enable the modifications due to the nonideality of the cement aqueous phase to be clearly demonstrated [6].

2.1. Origin of surface charge and Boltzmann distribution

Surface charge can originate from dissociation of surface groups, specific adsorption of ions or ionic polymers. The distribution of ionic species as a function of distance from a charged surface is calculated by assuming that the suspension is at equilibrium. This means that for each species, the electrochemical potential will be the same, whatever its distance from the charged surface. A word of caution must be made with respect to hydrating cement suspensions since these are not at full chemical equilibrium and the ionic composition evolves with time. However, locally, one might still reach an equilibrium condition in which ions have the same chemical potential in the bulk as close to the reacting surfaces. Over time, the nature of the exposed surfaces changes, so that the potential changes and that other ionic compositions will match this equilibrium requirement. Although these changes in the aqueous phase composition linked with the necessary hydration phenomenon are continuous, the overall change composition (e.g., between 6, and 180 min [7]) is not so drastic as to invalidate the current approach. For example, the data used later in the article for cement pore solutions are reasonably typical for samples after 3–5 h of water–cement contact for w/c ratios of 0.45. These data collected in 1997 by Yang et al. [8] compare very well with data collected by Longuet et al. [9] in 1973 and further data published by Longuet in 1976 [10] suggesting the approach, although specific, will apply generally. With this in mind, we proceed by using the equilibrium condition for the ionic species between the bulk and in the electrostatic field of cement particles. This can be written in the following manner:

$$\Delta\mu_k^* = \Delta\mu_k + ez_k\Delta\psi = k_B T\Delta\ln(a_k) + ez_k\Delta\psi = 0 \tag{1}$$

$$\Delta\ln(a_k) = -\frac{ez_k}{k_B T}\Delta\psi$$

where μ_k^* is the electrochemical potential of species k, μ_k is the chemical potential of species k, a_k is the activity of species k, z_k is the number of unit charges born by species k, ψ is the electrostatic potential at the point where μ_k^* is evaluated, e is the charge of an electron, k_B is the Boltzmann constant, and T is the temperature in kelvin.

At an infinite distance from the surface, it is assumed that the activity of all species is given by their bulk activity a_k^b. From Eq. (1), the probability of finding a species at a certain point from the surface in the potential field can be represented by the Boltzmann distribution. For ideal solutions, in which activity is given by concentration, this leads to the following expression [6]:

$$n_k = n_k^b \exp\left(-\frac{ez_k}{k_B T}\psi\right) \tag{2}$$

where n_k is the concentration of species k and n_k^{b} is the concentration of species k in the bulk.

For nonideal solutions, the activity a_k can be expressed by the product between the concentration n_k and an activity coefficient γ_k:

$$a_k = n_k\gamma_k = n_k^{\mathrm{b}}\gamma_k^{\mathrm{b}}\exp\left(-\frac{\mathrm{e}z_k}{k_{\mathrm{B}}T}\psi\right) \tag{3}$$

where γ_k is the activity coefficient of species k and γ_k^{b} is the activity coefficient of species k in the bulk.

This shows that in nonideal solutions, it is the activities rather than the concentrations that adopt a Boltzmann distribution.

2.2. Electric double layer and Poisson–Boltzmann equation

A charged interface attracts ions of opposite signs whereas Brownian motion will oppose this process, acting as a rehomogenizing force. The distribution of ions at a charged interface is described by the double layer model of Goüy–Chapman that distinguishes between two zones [6]. A first layer, called either the Stern layer or the compact layer, defines the thickness of adsorbed ions that are linked to the surface sufficiently strongly to be unaffected by Brownian motion. This layer can be considered as a capacitor in which the potential varies linearly with separation. The outer bound of this layer is considered to carry the charge, which is relevant for describing the next layer. A second layer, called the diffuse layer, covers the region from the outer bound of the Stern layer to the bulk solution, in which ions are affected both by Brownian motion and by the charged interface. The Stern layer and the diffuse layer are called the double layer. In an electrolyte, the Poisson equation takes the form:

$$\varepsilon\varepsilon_0\nabla^2\psi = -\rho^{(\mathrm{f})} \tag{4}$$

where $\rho^{(\mathrm{f})}$ is the volume density of free charges, ε_0 is the permittivity of vacuum, and ε is the relative dielectric constant of the medium between the particles.

For electrolyte concentrations less than 1 M and potentials less than 200 mV, the electrostatic potentials in the Poisson equation and the Boltzmann distribution can be considered identical [6]. The volume density of free charges is given by:

$$\rho^{(\mathrm{f})} = \sum_{k=1}^{N}\mathrm{e}z_k n_k \tag{5}$$

Substituting the Poisson equation, Eq. (4), and the Bolzmann equation for ideal solutions, Eq. (2), into Eq. (5), we obtain the Poisson–Boltzmann equation for ideal solutions:

$$\nabla^2\psi = -\frac{\mathrm{e}}{\varepsilon\varepsilon_0}\sum_{k=1}^{N} z_k n_k^{\mathrm{b}}\exp\left(-\frac{\mathrm{e}z_k}{k_{\mathrm{B}}T}\psi\right) \tag{6}$$

Note that potential and concentration, which are linked through in this equation, both depend on the distance from the charged interface.

For nonideal electrolytes, Eq. (3) is used in lieu of Eq. (2), leading to:

$$\nabla^2\psi = -\frac{\mathrm{e}}{\varepsilon\varepsilon_0}\sum_{k=1}^{N} z_k n_k^{\mathrm{b}}\frac{\gamma_k^{\mathrm{b}}}{\gamma_k}\exp\left(-\frac{\mathrm{e}z_k}{k_{\mathrm{B}}T}\psi\right) \tag{7}$$

Before attempting to solve for Eq. (7), we develop the case for the ideal solution. The result for symmetric electrolytes can be used to derive expressions for the force between charged particles. To use such expression, we will later show how a fitting routine may be used to express Eq. (7) by an equivalent ideal symmetric electrolyte.

2.3. Double layer at the surface of a sphere

While the Poisson–Boltzmann equation can be solved analytically for parallel planes, the situation is different for spheres. Indeed, the curvature leads to another expression of the left-hand term that complicates the resolution. Different approximations exist, most of which are concerned with symmetric electrolytes ($n_- = n_+$; $z_- = -z_+$). The Poisson–Boltzmann equation can be rewritten for a symmetric electrolyte as:

$$\nabla^2\psi = 2\frac{\mathrm{e}z_+ n_+^{\mathrm{b}}}{\varepsilon\varepsilon_0}\sinh\left(+\frac{\mathrm{e}z_+}{k_{\mathrm{B}}T}\psi\right) \tag{8}$$

Linearization of this expression, valid for small values of $(\mathrm{e}z_+/k_{\mathrm{B}}T)\psi$, leads to:

$$\nabla^2\psi \cong \frac{2\mathrm{e}^2 z_+^2 n_+^{\mathrm{b}}}{\varepsilon\varepsilon_0 k_{\mathrm{B}}T}\psi = \kappa^2\psi \tag{9}$$

which introduces the Debye length κ^{-1}:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon\varepsilon_0 k_{\mathrm{B}}T}{2\mathrm{e}^2 z_+^2 n_+^{\mathrm{b}}}} \tag{10}$$

For a nonsymmetric electrolyte, the Debye length is written:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon\varepsilon_0 k_{\mathrm{B}}T}{\sum_k \mathrm{e}^2 z_k^2 n_k^{\mathrm{b}}}} \tag{11}$$

3. Equivalent symmetric electrolyte

To facilitate the later calculations of interaction potentials between charged particles in cement suspensions, we attempt to express the right-hand side of Eq. (11) as if it were to describe an ideal symmetric electrolyte having the same Debye length but a nonunit charge. This means that we will use a fitting procedure that will provide us with a valence and concentration that would render Eqs. (7) and (8) identical for any potential. To achieve this, we first equate the Debye length of a symmetric electrolyte with that of a nonsymmetric electrolyte:

$$\sqrt{\frac{\varepsilon\varepsilon_0 k_\mathrm{B} T}{2\mathrm{e}^2 z_+^2 n_+^\mathrm{b}}} = \sqrt{\frac{\varepsilon\varepsilon_0 k_\mathrm{B} T}{\sum_k \mathrm{e}^2 z_k^2 n_k^\mathrm{b}}} \tag{12}$$

$$z_+^2 n_+^\mathrm{b} = \frac{\sum_k z_k^2 n_k^\mathrm{b}}{2} \tag{13}$$

In order to describe the Poisson–Boltzmann equation by an equivalent symmetric electrolyte, we equate Eqs. (8) and (7):

$$2\frac{\mathrm{e}z_+ n_+^\mathrm{b}}{\varepsilon\varepsilon_0}\sinh\left(+\frac{\mathrm{e}z_+}{k_\mathrm{B}T}\psi\right) = -\frac{\mathrm{e}}{\varepsilon\varepsilon_0}\sum_{k=1}^{N} z_k n_k^\mathrm{b}\frac{\gamma_k^\mathrm{b}}{\gamma_k}\exp\left(-\frac{\mathrm{e}z_k}{k_\mathrm{B}T}\psi\right) \tag{14a}$$

Giving Eq. (14b)

$$z_+ n_+^\mathrm{b}\sinh\left(+\frac{\mathrm{e}z_+}{k_\mathrm{B}T}\psi\right) = -\frac{1}{2}\sum_{k=1}^{N} z_k n_k^\mathrm{b}\frac{\gamma_k^\mathrm{b}}{\gamma_k}\exp\left(-\frac{\mathrm{e}z_k}{k_\mathrm{B}T}\psi\right) \tag{14b}$$

Substituting Eq. (13) into Eq. (14b) we get:

$$\frac{\sinh\left(+\frac{\mathrm{e}z_+}{k_\mathrm{B}T}\psi\right)}{z_+} = \frac{-\sum_{k=1}^{N} z_k n_k^\mathrm{b}\frac{\gamma_k^\mathrm{b}}{\gamma_k}\exp\left(-\frac{\mathrm{e}z_k}{k_\mathrm{B}T}\psi\right)}{\sum_k z_k^2 n_k^\mathrm{b}} \tag{15}$$

For any suspension at a given time, z_k and n_k^b can be determined experimentally. The activity coefficients of the bulk solution γ_k^b can be evaluated using an appropriate model for ion activities (see below). To solve Eq. (15) for z_+, we first need to relate the activity coefficients γ_k of the ions subjected to the electrostatic potential ψ. This would leave z_+ as a function of ψ. In a fitting procedure described later, we identify the value of z_+ that minimize errors of the largest possible range of potentials in a suspension of specified ionic composition, taken as a numerical illustration of this approach.

4. Nonideality of cement suspension

4.1. Expressions for activity coefficients

For dilute solutions, activity coefficients are equal to unity, and concentrations suffice. However, this description fails for ionic strengths of the order of 10^{-3} M. Debye and Hückel first proposed the calculation of ion activities valid up to about an ionic strength of 10^{-2} M using:

$$\log_{10}(\gamma_k) = -\frac{A_\mathrm{D-H} z_k^2\sqrt{I}}{1 + a_k^0 B_\mathrm{D-H}\sqrt{I}} \tag{16}$$

where $I = \frac{1}{2}\sum_k z_k^2 n_k$, z_k is the charge number of the ion k, n_k is the concentration of the ion k, a_k^0 is the Debye–Hückel radius of the ion k, $A_\mathrm{D-H}$ and $B_\mathrm{D-H}$ are the Debye–Hückel constants, and I is the ionic strength of the solution. Introducing a third Debye–Hückel, $C_\mathrm{D-H}$, parameter allows its use up to about 10^{-1} M.

$$\log_{10}(\gamma_k) = -\frac{A_\mathrm{D-H} z_k^2\sqrt{I}}{1 + a_k^0 B_\mathrm{D-H}\sqrt{I}} + C_\mathrm{D-H}\sqrt{I} \tag{17}$$

For further extension, a species-specific parameter, C_k, must be used, which allows predictions to be made up to 1 M (at 25 °C):

$$\log_{10}(\gamma_k) = -\frac{A_\mathrm{D-H} z_k^2\sqrt{I}}{1 + a_k^0 B_\mathrm{D-H}\sqrt{I}} + C_k\sqrt{I} \tag{18}$$

For the ionic strengths of the cement suspensions considered later, the second version of the extended Debye–Hückel model Eq. (18) was considered most suitable. A more accurate and recent model proposed by Pitzer [11] was not used, because the data base does not account for the formation of ion pairs such as $\mathrm{Ca(OH)^+}$ that can substantially modify the expected calcium distribution at and away from the surface.

To illustrate the distribution of ionic species in an aqueous phase, ion activity calculations have been made using data reported by Yang et al. [8] (Table 1) for w/c ratios of 0.35 and 0.45 (180 min contact time). The main aim in presenting these ion activity calculations is to obtain the relative distribution of the different aqueous species in order to perform correct calculations of electrostatic interactions between particles. We can therefore neglect the species associated with Mg, Al, and Si, because their low concentrations contribute little to the ionic strength.

To perform the activity calculations, we have used the initial equilibration step included in the program KINDIS initially developed by Fritz [12]. While performing these calculations, it turns out that for the indicated pH, the solution is not electrically neutral. The use of a program integrating activity coefficients was needed for this, since pH is a measure of the activity of $\mathrm{H^+}$ from which the

Table 1
Ionic concentrations (mmol/kg) for two cement suspensions as reported by Yang et al. [8]

w/c	$\mathrm{K^+}$	$\mathrm{Na^+}$	$\mathrm{Ca^{2+}}$	$\mathrm{SO_4^{2-}}$	$\mathrm{Si^{4+}}$	$\mathrm{Mg^{2+}}$	$\mathrm{Al^{3+}}$	$\mathrm{OH^-}$	pH
0.35	123.94	28.14	18.31	58.72	0.05	0.04	0.07	70.79	12.85
0.45	119.60	27.12	22.28	50.34	0.4	0.02	0.09	93.3	12.97

Ionic strengths are 266.3 and 268.9 mmol/kg.

Table 2
Recalculated distributions of ionic species (mmol/kg) in a cement suspension at 25 °C

	K^+	Na^+	Ca^{2+}	OH^-	SO_4^{2-}	KSO_4^-	$NaSO_4^-$	$Ca(OH)^+$	$CaSO_4$	pH
Concentration (mmol/kg H_2O)	115.75	25.11	8.68	67.86	41.28	8.19	3.08	3.45	6.17	12.69
Activity coefficient	0.695	0.745	0.347	0.717	0.255	0.717	0.736	0.729	1.052	
Total (mmol/kg H_2O)	123.94	28.19	18.31	71.31	58.72	–	–	–	–	
% of total ion in dissociated form	93	89	47	95	70	–	–	–	–	

w/c = 0.35. Ionic strength is 211.6 mmol/kg.

activity of OH^- but not its concentration can be calculated. The solution bears an excess of anions, which is attributed to the low quality of pH measurements in highly alkaline solutions. The pH, which leads to electric neutrality, has therefore been recalculated (± 0.01 pH units). After this calculation, the program automatically balances any remaining small charge excess by adding Na^+. The results are presented in Tables 2 and 3. The last line in Tables 2 and 3 indicates the percentage of each element found in its fully dissociated state. It can be seen for instance that less than half the calcium is found in its divalent form. In addition, a substantial amount of sulfate forms pairs with the cations present in solution. All these ion associations reduce the ionic strength. An ionic strength calculated ignoring these ion pairs—assuming full ionization of each species results in an overevaluation of 26%. The activity coefficients of all ions are substantially different from unity illustrating the nonideal nature of the cement aqueous phase.

4.2. Potential dependent activities

The approach outlined above can provide the bulk activity coefficients for cement suspensions at any time a solution analysis is performed. Using the bulk activity coefficients, it is possible to calculate, from Eq. (3), the activity of all the species as a function of the electrostatic potential using an iterative procedure (obtaining both concentration and activity). First the ionic strength is calculated with the bulk concentration of electrolytes and with the data in Table 4, a first approximation of activity coefficients can be obtained with the Debye–Hückel relationship (Eq. (18)). A new set of concentrations is thus obtained and the procedure is then repeated with this new set of concentrations until sufficient convergence is obtained (in our case 0.1% between two consecutive steps). As a result, one can express the ionic strength as a function of the local electrostatic potential, which in turn allows the calculation to be made for any local activity coefficient.

This is illustrated in Fig. 1, with a plot of ionic strength versus the local electrostatic potential and it is seen to vary by a factor of six over the range investigated. For the w/c = 0.35 suspension, we report in Fig. 2 the error induced if ideal solutions are assumed. For the purpose of this comparison, the total concentrations of the primitive ions are given. In addition, only values for opposite ion sign and surface potential are shown (Ca^{2+}, K^+, and Na^+ are given for negative potentials, while SO_4^{2-} and OH^- are given for positive potentials only). Indeed, when ion and potential have the opposite sign, the local ion concentration goes to zero and the relative error diverges. In this figure, it appears that it is mainly the concentration of the divalent ions (which have not formed ion pairs) that is biased if an ideal solution is assumed.

4.3. Fitting of the equivalent symmetric electrolyte

At this point, we have all that is needed to identify the valence and concentration of our equivalent symmetric electrolytes. For our examples, however, we must still distinguish between positive and negative potentials, because of the nonsymmetric character of the liquid phase demonstrated above. To solve Eq. (15) for the noninteger charge number z, a mean square minimization was used for a series of values at a resolution of 5 mV. Computations were performed over the range found to fall within the limit of ionic strengths less than unity (0 to 20 mV and 0 to − 35 mV). Results are shown in Table 5 and indicate values very similar to those for 1:1 and 3:3 symmetric electrolytes for the negative and positive potentials, respectively. A graphic comparison of the values for the right-hand term of Poisson–Boltzmann equation is shown for positive potentials in Fig. 3 and for negative potentials in Fig. 4. Open triangles

Table 3
Recalculated distribution of ionic species (mmol/kg) in cement suspension at 25 °C

	K^+	Na^+	Ca^{2+}	OH^-	SO_4^{2-}	KSO_4^-	$NaSO_4^-$	$Ca(OH)^+$	$CaSO_4$	pH
Concentration (mmol/kg H_2O)	112.91	25.77	10.82	87.40	34.56	6.69	2.65	5.54	6.45	12.8
Activity coefficient	0.695	0.745	0.348	0.717	0.256	0.717	0.736	0.729	1.052	
Total (mmol/kg H_2O)	119.60	28.42	22.80	92.94	50.34	–	–	–	–	
% of total ion in dissociated form	94	91	47	94	69	–	–	–	–	

w/c = 0.45. Ionic strength is 211.2 mmol/kg.

Table 4
Parameters for calculating ion activities of selected aqueous species

	K^+	Na^+	Ca^{2+}	OH^-	SO_4^{2-}	KSO_4^-	$NaSO_4^-$	$Ca(OH)^+$	$CaSO_4$
a_k^0	3.0	4.0	6.0	3.5	4.0	3.5	4.3	4.0	4.0
C_k	0.0163	0.0867	0.1546	0.041	*−0.04*	0.041	0.041	0.041	0.041

show exact values using all ionic species and activities. The dashed line shows the calculated equivalent symmetric electrolyte. Closed triangles show values obtained if a nonideal solution is assumed but the effect of potential is not considered. Finally, the continuous line shows the Debye–Hückel approximation assuming the solution to be ideal and not calculating the distribution of the various ionic species. For negative surface potentials, it appears that the Debye–Hückel approximation applied to the Poisson–Boltzmann equation in which an ideal solution is assumed, induces minor errors down to −30 mV but fails above 10 mV for positive surface potentials. Since most reported measurement of potentials for cement suspensions fall within this range [8] previous studies using the ideal solution assumptions are valid within the mean field approach.

5. Electrostatic force—effect of nonideal electrolyte solutions

In the previous section, we have shown how the aqueous phase of a cement suspension affects the potential derived from the Poisson–Boltzmann equation because of its nonideal solution behavior. We shall now show how to evaluate the implications of such deviations on the repulsive electrostatic force between two spherical particles in cement suspensions. To do this, we first have to provide a charge–potential relationship, taking into account surface potential regulation and the aqueous phase solution nonideality.

5.1. Charge–potential relation

For values of $\kappa r > 0.5$, there is a relationship between the charge density and the surface potential, which gives less than 5% error (see Ref. [6], chap. 4.8).

$$q = \frac{Q}{4\pi r^2} = \frac{\varepsilon\varepsilon_0 k_B T}{ez}\kappa\left[2\sinh\left(\frac{1}{2}\Psi_s\right) + \frac{4}{\kappa r}\tanh\left(\frac{1}{4}\Psi_s\right)\right] \tag{19}$$

where $\Psi_s = ez\psi_s/k_B T$. This expression includes a dependence on particle radius, r. However, for the range of particle sizes of interest in cement, this dependence is not significant, leading to:

$$q = \frac{Q}{4\pi r^2} \cong 2\frac{\varepsilon\varepsilon_0 k_B T}{ez}\kappa\sinh\left(\frac{1}{2}\Psi_s\right) \tag{20}$$

The error induced by this approximation is less than 0.5% for particles with radii between 0.1 and 25 μm and for surface potentials up to 50 mV.

5.2. Surface potential regulation

So far, we have looked at relations between local electrostatic potential in the aqueous phase of a dielectric. Through the Boltzmann distribution, this local potential could be related to the local composition of the solution, which has been described as a nonideal electrolyte. Here, we try to relate the surface potential to the bulk composition of the electrolyte, based on the assumption that the particle

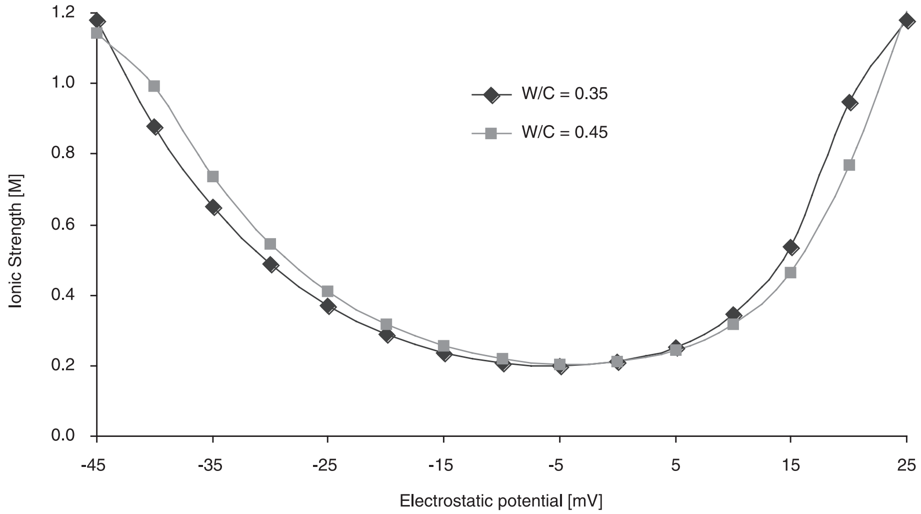

Fig. 1. Variation of ionic strength as a function of local electrostatic potential for two different w/c ratios.

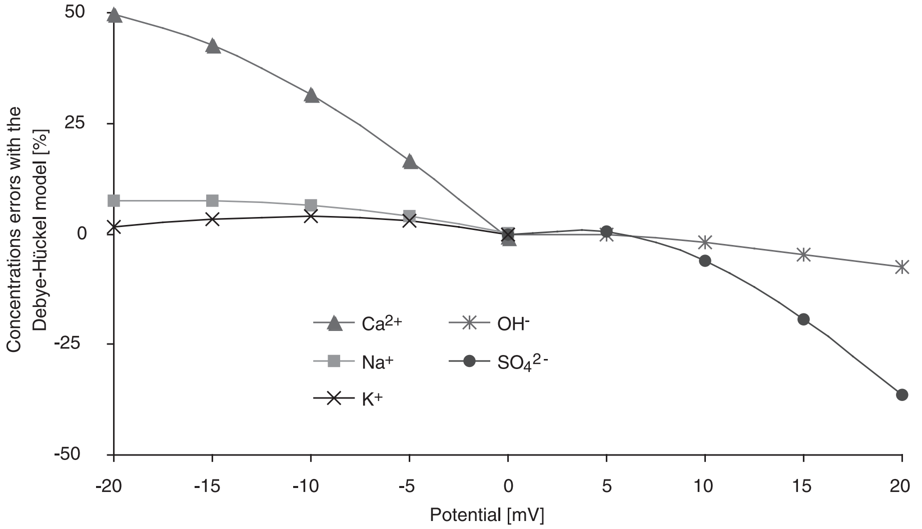

Fig. 2. Relative percentage of error made if an ideal rather than a nonideal is assumed to calculate the ion distribution of the aqueous phase of a cement suspension (w/c = 0.35).

surface has ionizable groups. The extent of their ionization will dictate the value of the surface potential. It is also assumed, that these groups are in equilibrium with the solution. For the purpose of discussing the effect of adsorbed superplasticizers, let us consider an adsorbed polymer having sodium sulfonate groups. We have:

$$\mathrm{R-SO_3Na} \rightleftarrows \mathrm{R-SO_3^-} + \mathrm{Na^+} \tag{21}$$

with

$$K_{\mathrm{R-SO_3Na}} = \frac{a_{\mathrm{R-SO_3^-}} a^{\mathrm{o}}_{\mathrm{Na^+}}}{a_{\mathrm{R-SO_3Na}}} \tag{22}$$

The superscript o indicates that the activity of Na^+ is evaluated at the surface. In addition to association–dissociation equilibrium of sodium with sulfonate groups, other counter-ions must also be considered. We therefore have:

$$\mathrm{R-SO_3K} \rightleftarrows \mathrm{R-SO_3^-} + \mathrm{K^+} \tag{23}$$

$$\mathrm{(R-SO_3)_2Ca} \rightleftarrows 2\mathrm{R-SO_3^-} + \mathrm{Ca^{2+}} \tag{24}$$

$$\mathrm{R-SO_3CaOH} \rightleftarrows \mathrm{R-SO_3^-} + \mathrm{Ca(OH)^+} \tag{25}$$

At this point, we approximate the activities of the surface species to their surface concentrations. Therefore, the total number of sulfonate groups $[n_{\mathrm{R-SO_3}}]$ per unit area is given by:

Table 5
Characteristics of calculated equivalent symmetric noninteger electrolytes and range of potentials for which the ionic strength is less than 1 mol/kg

	Potential	
	0 → − 35	0 → 20
Calculated equivalent symmetric electrolyte		
z	1.16	3.52
κ^{-1} (nm)	0.67	0.67
Debye–Hückel 1:1		
z	1	1
κ^{-1} (nm)	0.60	0.60

$$[n_{\mathrm{R-SO_3}}] \cong a_{\mathrm{R-SO_3^-}} + a_{\mathrm{R-SO_3Na}} + a_{\mathrm{R-SO_3K}} + a_{\mathrm{R-SO_3CaOH}} + a_{\mathrm{(R-SO_3)_2Ca}} \tag{26}$$

Substituting the equilibrium equations Eqs. (21) and (23)–(24) into Eq. (26), we get

$$[n_{\mathrm{R-SO_3}}] \cong a_{\mathrm{R-SO_3^-}} \left(1 + \frac{a^{\mathrm{o}}_{\mathrm{Na^+}}}{K_{\mathrm{R-SO_3Na}}} + \frac{a^{\mathrm{o}}_{\mathrm{K^+}}}{K_{\mathrm{R-SO_3NK}}} + \frac{a^{\mathrm{o}}_{\mathrm{CaOH^+}}}{K_{\mathrm{R-SO_3CaOH}}}\right) + a^2_{\mathrm{R-SO_3^-}} \frac{a^{\mathrm{o}}_{\mathrm{Ca^{2+}}}}{K_{\mathrm{(R-SO_3)_2Ca}}} \tag{27}$$

This equation can be solved for the activity of the dissociated surface sulfonate groups. Of the two roots of this equation, only the positive one has physical relevance. We get:

$$a_{\mathrm{R-SO_3^-}} = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$$

$$a = \left(1 + \frac{a^{\mathrm{o}}_{\mathrm{Na^+}}}{K_{\mathrm{R-SO_3Na}}} + \frac{a^{\mathrm{o}}_{k^+}}{K_{\mathrm{R-SO_3NK}}} + \frac{a^{\mathrm{o}}_{\mathrm{CaOH^+}}}{K_{\mathrm{R-SO_3CaOH}}}\right)$$

$$b = \frac{a^{\mathrm{o}}_{\mathrm{Ca^{2+}}}}{K_{\mathrm{(R-SO_3)_2Ca}}}$$

$$c = -[n_{\mathrm{R-SO_3}}] \tag{28}$$

Using the Boltzmann equation to calculate the ion potentials at the interface and multiplying by the electron charge yields the surface charge:

$$q = -\mathrm{e}a_{\mathrm{R-SO_3^-}} \tag{29}$$

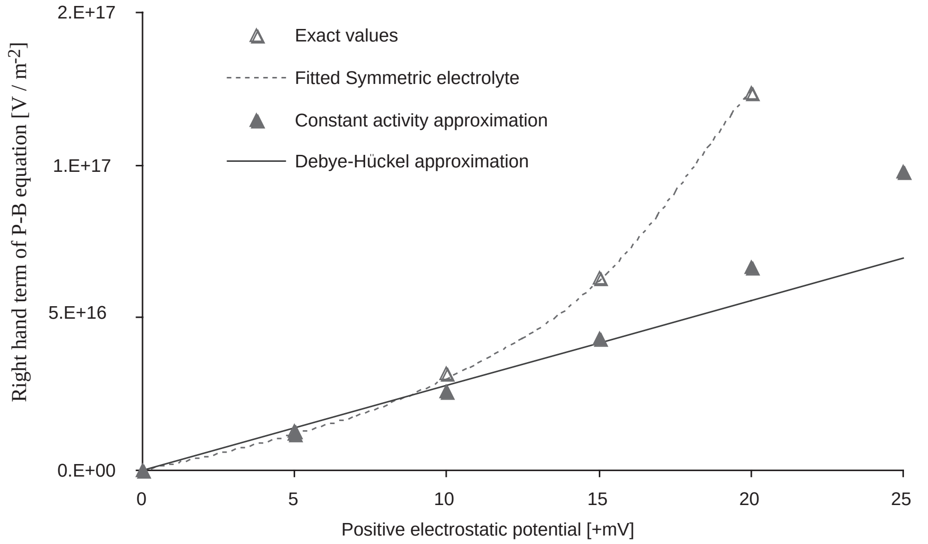

Fig. 3. Comparison of different representations of right-hand term of Poisson–Boltzmann equation for positive potentials.

This provides an additional relation between surface charge q and surface potential ψ_s. Equating Eqs. (29) and (20), we obtain:

$$2\frac{\varepsilon\varepsilon_0 k_B T}{ez_+}\kappa\sinh\left(\frac{1}{2}\frac{ez_+}{k_B T}\psi_s\right) = -ea_{R-SO_3^-} \tag{30}$$

Note that the left-hand term is calculated from the data for the equivalent symmetric electrolyte, while the term on the right side must be calculated with all counter-ions. This development leaves two unknowns, the surface concentration of sulfonate groups and the surface potential. For particles onto which ionic polymers are adsorbed, the surface concentration of ionic groups is linked to the surface coverage. A crude estimate would be to calculate this directly from adsorption data and knowledge of the number of ionic groups per adsorbed polymer. Whatever the exact relation between surface coverage and concentration of ionic groups, Eq. (30) indicates the surface potential should remain constant when particles approach, provided that no desorption occurs. This constitutes a basis for supporting the choice of a constant surface potential as a boundary condition for calculating electrostatic repulsion between particles. Note that the surface potential in Eq. (30) is the one at the outer bound of the Stern layer. This potential should be equal to or greater than the experimentally measurable zeta potentials. Other boundary conditions can

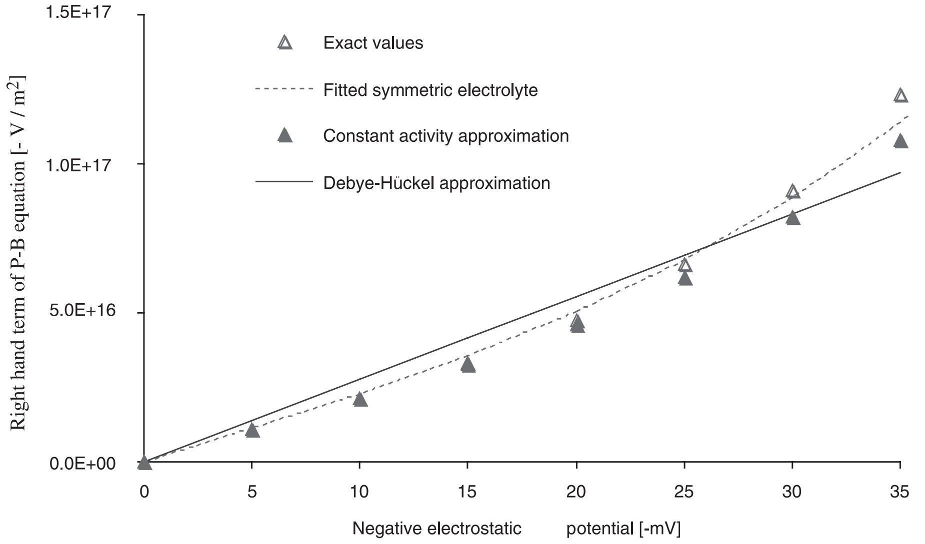

Fig. 4. Comparison of different representations of right-hand term of Poisson–Boltzmann equation for negative potentials.

be chosen (but are not within the scope of this article) such as constant surface charge or charge regulation (in which the criterion is electric neutrality between fluid and surfaces).

A similar treatment for surfaces of cement particle without adsorbed polymers would also lead to the conclusion that constant potential is a reliable condition to assume when considering the approach of two particles. In this case however, the ongoing reactions modify more drastically over time the ratio of exposed phases as well as the ionic composition of the aqueous phase, which means that one must be more cautious in extrapolating behavior from limited number of analysis of solution compositions. However, if the new surface phases are of the same nature, then this will tend to homogenize the types of surfaces and thus help in the simplified approach taken here.

5.3. General expression for electrostatic force between spheres with constant potential

The force expression for two charged spheres is given by:

$$\mathrm{F} = 2k_{\mathrm{B}}Tn_{+}^{\mathrm{b}}\int_{S}\left[1-\cosh\left(\frac{\mathrm{e}z_{k}}{k_{\mathrm{B}}T}\psi_{x}\right)\right]\mathrm{n}\mathrm{d}S + \varepsilon\varepsilon_{0}\int_{S}\left[\mathrm{EE}-\frac{1}{2}\mathrm{E}\cdot\mathrm{Ed}\right]\mathrm{n}\mathrm{d}S \qquad (31)$$

To obtain the electrostatic force between two spheres in a symmetric electrolyte, the approximation of Vellegrol [13] was used and is treated in detail elsewhere [14]. One interesting aspect of Vellegrol's approach is that the radius used to describe the interaction is the harmonic radius ($r = 2r_1r_2/(r_1+r_2)$) and not the median volume diameter so

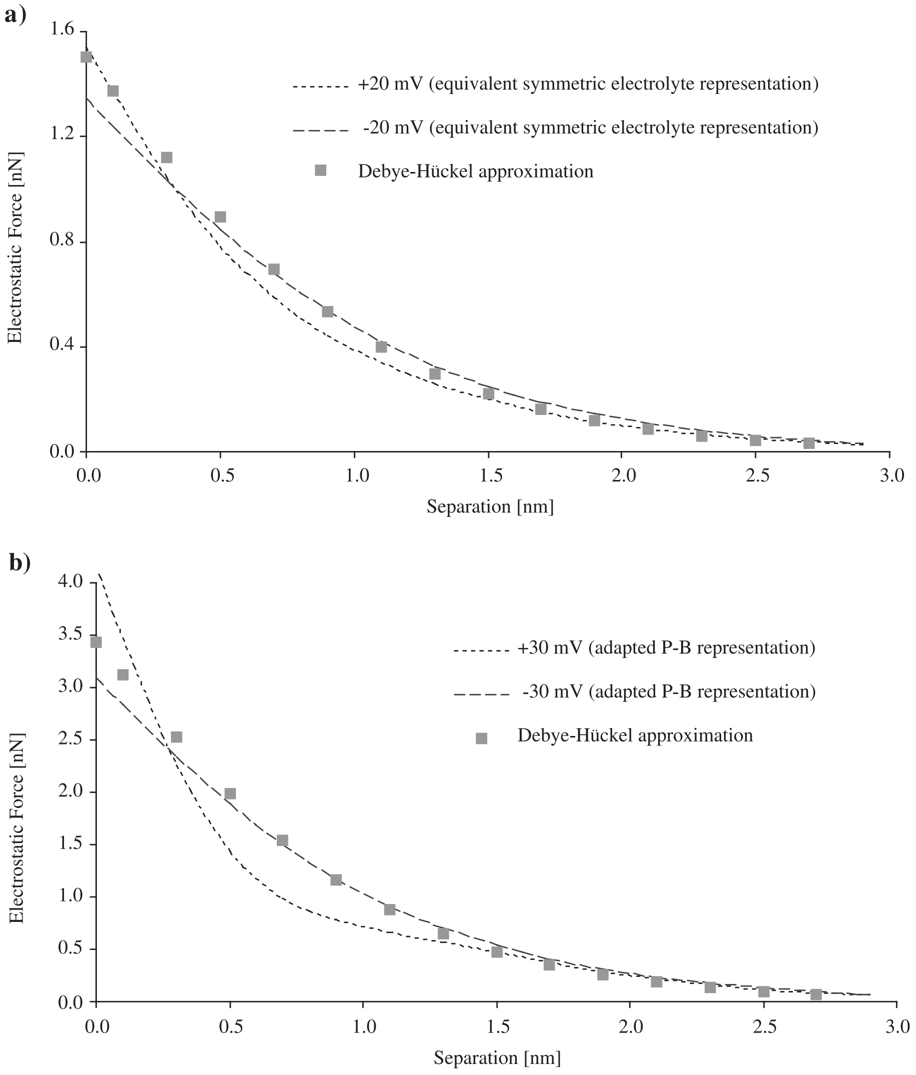

Fig. 5. Electrostatic force between spherical calcite particles having 1 μm radius and surface charge of (a) 20 and (b) 30 mV. The Debye–Hückel approximation is compared with exact results for the equivalent symmetric electrolyte determined for thermodynamics of the nonideal cement suspension.

often used in interparticle force calculations. The harmonic radius was also found to be the natural way of describing interaction energies taking into account pairwise interactions between different size particles in a distribution and is an important aspect in the goal of calculating quantitative interaction energies from first principles [14].

5.4. Electrostatic force between equally charged spheres

We consider two calcite particles with 1 μm radius, 20 mV surface potentials, and an aqueous phase similar to a cement suspension. In such a situation, as discussed previously, we must use different equivalent symmetric electrolytes to distinguish the positive from the negative potential situations. In addition, we use the Debye–Hückel approximation for a 1:1 electrolyte and neglect any effect of the nonideal thermodynamics. In this case, the repulsive force is predicted to be the same whether both surfaces are positive or negative. Using Eq. (31), values for all three situations are compared in Fig. 5. The first observation is that whatever the situation, the order of magnitude is well predicted by the Debye–Hückel approximation. At contact, this approximation tends to overevaluate the force for the negative potential by about 15%. On the other hand for the positive potentials, errors are greater at intermediate separations. At ±30 mV these trends are more pronounced.

One of the limitations to this mean field approach lies in the failure to predict any ion pairing interactions between negatively charged surfaces through divalent calcium. However, it must be noted that only half the calcium is present in divalent form and that majority (~ 93%) of cations in the solution are monovalent (for the anions ~ 76% are monovalent). Another limitation of the mean field double layer model is that it assumes continuity of point charges. However, owing to the high concentration of electrolytes in cement suspensions, the size of the double layer becomes comparable to that of the ions. Only more sophisticated approaches can adequately address both these limitations, through computer intensive calculations such as those done by Pellenq et al. [5]. This would lead to the development of a more quantitative evaluation of the magnitude of the electrostatic contribution to dispersion and help in the general objective for predicting superplasticizer performances. However, the use of the approach described in this article and the repulsive forces that arise from charged surfaces has been made [14]. For the case of real cement suspensions with added superplasticizer, the approach has shown very encouraging results with respect to yield stress predictions using this fundamental approach to calculate interparticle forces.

6. Conclusions

The distribution of different ionic species in the nonideal electrolyte of cement suspensions can be used to calculate the concentration and unit charge (noninteger) of an equivalent symmetric electrolyte. The condition for this approach to be valid is that the solution of the Poisson–Boltzmann equation for the symmetric electrolyte and the aqueous phase of a cement suspension are identical. This provides a more simple and exact description of the local electrostatic potential at a certain distance from cement particles. The interest in defining a symmetric electrolyte is that well-established approximations for electrostatic force can then be used. It turns out the potential cannot be described in the same way owing to the fact that the cement suspension is not a symmetric electrolyte. In fact, for the region of negative potentials, which is of particular interest for cement suspensions dispersed with organic additives, the calculation leads to a result almost equivalent to that of a 1:1 electrolyte. For the positive potential range, the situation resembles that of a 3:3 electrolyte. These effects, however, are only of second and higher orders in the expression of the electrostatic force. It turns out that the repulsive force is relatively well described by the Debye–Hückel approximation for the cement suspensions used in this study. These calculations indicate that for negatively charged surfaces the Debye–Hückel approximation for calculating interparticle forces provides a good approximation (within 15%) despite the high degree of nonideality of the cement aqueous phase solutions (up to 50%). For positively charged surfaces, the essentially nonsymmetric character of the electrolyte in the aqueous phase leads to more consequent deviations. This however is not too problematic since all reported commercial superplasticizers are anionic. The numerical illustrations of this approach are related to a specific cement (typical for about 3 h contact with water) but the above results are expected to be general. These results help increase our confidence in using a fundamental approach towards understanding superplasticizer effects in cements—albeit with the need for more detailed understanding of superplasticizer conformation and charge distribution at the surface of the cement particles, especially when one considers the nonspherical shape and consequent charge and phase inhomogeneities that may further influence interactions.

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