Overcoming electroneutrality: concentrative and electrical conditions inside a charged droplet of electrolyte solution

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Abstract

For the geometry of a spherical droplet carrying ionic charges, a solution to the Poisson–Boltzmann equation can be found via two routes: by numerical simulation and as an algebraic series. The maximum charge is limited by the surface tension of the liquid according to Rayleigh’s law. Potential and ionic concentration profiles have been determined for a variety of electrolytes in aqueous solution, emphasizing charges of a magnitude that just meet the Rayleigh criterion for several droplet radii. The charge is found to occupy a diffuse layer, contrasting with the frequent assumption that the charge resides on the droplet’s surface. Under conditions that have been delineated, the charge consists solely of ions sharing the sign of the droplet’s charge, counterions being absent. © 2002 Published by Elsevier Science B.V.

Keywords: Electroneutrality; Rayleigh limit; Charged droplets; Poisson–Boltzmann distribution

1. Introduction

Mildly charged droplets of aqueous electrolyte solution occur in such natural phenomena as fogs and sea-spray. Much larger charges are encountered in many of the technologies—microspray cleaning [1,2], fuel atomization, electrohydrodynamic powder production [3], ink jet printing and electrospray mass spectrometry [4]—that employ streams of liquid droplets. In some of these processes the droplets are of submicron sizes. Drops of conducting liquids are often considered to carry the charge on their surfaces and, while this is often close to being the truth, a Poisson–Boltzmann analysis of the distribution of ions within the spherical droplet will provide a more accurate description. Such an analysis is carried out in this paper. It will be shown that the distribution of charge in an aqueous droplet is quite diffuse and that charge is never localized entirely on the drop’s surface, as it would be on a perfectly conducting fluid. Part of the charge arises from an enrichment, compared with the bulk solution from which the droplets form, of the ions which share the sign of the droplet’s charge. The remainder is due to expulsion of the counterions. We shall investigate the extent of these two processes at all points in the droplet, as well as determining the distributions of charge and electrical potential.

In most of the technologies cited above, charged drops of small size are created by a process, the principle of which is replicated in the apparatus illustrated in Fig. 1. Under the force generated by the pressure difference, a dilute aqueous electrolyte solution feeds

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down a narrow insulating capillary into a vacuum chamber. It is atomized at the exit nozzle and, on account of the very high voltage applied, the droplets produced are small and charged. Droplet generation rates in the range $10^9-10^{13}$ per second can be achieved [1]. The droplets travel at high speed in a jet. In the diagram, this jet impinges on a metallic collector plate, where the droplets are neutralized. Though it is an unusual one, the procedure is basically an electrolysis experiment, and if the polarity is as diagramed, the droplets are positively charged and the collector plate serves as the cathode. Because it will be assumed that the solute is a binary electrolyte, neither ion of which is electroactive, then the reaction that occurs at the collector plate will be

$$e^{-} + H_2O(l) \rightarrow OH^{-}(aq) + \frac{1}{2}H_2(g)$$

(1)

The extent to which this reaction occurs will depend on $(z_+, N_+ + z_- N_-)$, the excess number of cationic charges over anionic charges in the droplet, and on $v$, the number of droplets formed per second. In fact, the steady current will be

$$I = Q_e v (z_+ N_+ + z_- N_-)$$

(2)

where $Q_e$ is the elementary charge $(1.602177 \times 10^{-19}$ C), $z_\pm$ are the charge numbers of the two ions and $N_\pm$ are the numbers of cations or anions per droplet.

2. Relating drop composition to feed solution concentration

A term $C$, defined as

$$C = z_+ c_+ = - z_- c_-$$

(3)

where $c_\pm$ are the ionic concentrations (mol m$^{-3}$), will be used to characterize the concentration of the bulk electrolyte solution. $C$ denotes the concentration of the feed solution in the old-fashioned ‘normality’ or ‘equivalents per unit volume’ units. The number densities (m$^{-3}$) of cations and anions in this feed solution are given by

$$(n_\pm)_{\text{feed}} = \frac{\pm LC}{z_\pm}$$

(4)

where $L$ denotes Avogadro’s (or L"oschmidt’s) constant $(6.02214 \times 10^{23}$ mol$^{-1}$).

If $R$ is the radius of the droplet and $A$ is the cross-sectional area of the capillary, the velocity (m s$^{-1}$) of solution down the capillary is given by

$$v = \frac{4\pi R^3}{3A}$$

(5)

if we ignore any dispersion of droplet sizes. The velocity will vary parabolically across the capillary’s bore but Eq. (5) gives the average velocity. If the droplets are positively charged, then cations move down the capillary toward the nozzle at a faster rate than the solution itself and their speed can be calculated from the fact that $vN_+$ cations leave the capillary per second. The cation speed can be found by dividing this escape rate by the cation number density and by the capillary’s cross-sectional area. Thus

$$vN_+ = \frac{z_+ vN_+}{LCA}$$

(6)

where, in the second step, use was made of Eq. (4). The additional velocity of the cations compared with the solution, that is, the difference between the velocities in Eqs. (6) and (5) is caused by their migration in the field existing along the capillary and is proportional to the field strength and to the mobility of the cation; thus

$$z_+ vN_+ = \frac{4\pi R^3}{3A} \text{migration} = - u_+ \frac{d\phi}{dx}$$

(7)

Conversely, the anions move more slowly towards the nozzle than does the solution and their (negative) migration velocity is analogously

$$- z_- vN_- = \frac{4\pi R^3}{3A} \text{migration} = u_- \frac{d\phi}{dx}$$

(8)

The previous two equations may be divided and solved for $C$, producing the result

$$C = \frac{3(z_+ u_+ N_+ - z_- u_- N_-)}{4\pi L(u_+ + u_-)R^3}$$

(9)

which relates the concentration of the feed solution to the composition of the droplets.

The total charge on the droplet depends on the numbers of cations and anions according to the equation

$$Q = (z_+ N_+ + z_- N_-)Q_e$$

(10)

which may be combined with Eq. (9) to eliminate either $N_-$ or $N_+$. The result, in either case, is

$$N_\pm = \frac{u_\pm Q}{z_\pm(u_+ + u_-)Q_e} \pm \frac{4\pi LR^3 C}{3z_\pm} = \frac{t_\pm Q}{z_\pm Q_e} \pm \frac{4\pi LR^3 C}{3z_\pm}$$

(11)

where $t_\pm$ is the transport number of the ion in question.

Note that, in suitable circumstances, it is possible for one of the ions to be completely absent. For example,
the droplet will contain only cations if \( N_\text{c} = 0 \) which, according to Eq. (11), requires that

\[
\frac{Q}{C} = \frac{4\pi FR^4}{3z}\tag{12}
\]

where \( F \) denotes Faraday’s constant (\( LQ_e = 96485.3 \text{ C mol}^{-1} \)).

The mutual repulsion of charges, of either sign, on a liquid droplet tends to expand the area of the drop’s surface, thereby opposing the surface tension of the liquid | gas interface, which seeks to contract the surface. Thus, for a given radius \( R \), there exists a limit \( Q \) to the charge \( C \) of a droplet, isolated in and a vacuum or gas-phase environment, given by Rayleigh’s formula [5,6]

\[
|Q| \leq 8\pi \sqrt{\epsilon_0 \sigma R^3}\tag{13}
\]

where \( \sigma \) is the surface tension (close to 0.07198 N m\(^{-1}\) for water and dilute aqueous solution at 298 K) and \( \epsilon_0 \) is the permittivity (8.85419 × 10\(^{-12}\) F m\(^{-1}\) for vacuum and gases at low pressure)\(^2\). Though Rayleigh’s formula was derived for the case in which the entire charge \( Q \) is confined to the droplet’s surface, it may be shown (see Appendix A) that the same formula holds for any spherically symmetrical charge distribution. One consequence of the Rayleigh limit is that no more than about 4000 elementary charges may be present on an aqueous droplet of 0.1 \( \mu \text{m} \) radius. For a positively charged droplet of this size, the number 4000 usually represents the excess of cations over anions. In the special case of a feed concentration of \( C = 0.78 \text{ mM} \), and if \( t_+ = 0.5 \), there will be 4000 cations and no anions. For \( C < 0.78 \text{ mM} \), the Rayleigh criterion cannot be met for a droplet as small as 0.1 \( \mu \text{m} \) in radius.

Combining Eqs. (12) and (13) we arrive at

\[
C \leq \frac{6t_+}{F} \sqrt{\epsilon_0 \sigma R^3}\tag{14}
\]

This gives the range of feed concentrations for which a droplet of radius \( R \) can achieve the Rayleigh limit. It corresponds to anions being totally absent from the droplet. Table 1 lists a number of concentrations calculated by this formula.

<table>
<thead>
<tr>
<th>( R ) [( \mu \text{m} )]</th>
<th>( C ) [eq m(^{-3})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>24.8</td>
</tr>
<tr>
<td>0.03</td>
<td>4.78</td>
</tr>
<tr>
<td>0.1</td>
<td>0.785</td>
</tr>
<tr>
<td>0.3</td>
<td>0.151</td>
</tr>
<tr>
<td>1</td>
<td>0.0248</td>
</tr>
<tr>
<td>3</td>
<td>0.00478</td>
</tr>
<tr>
<td>10</td>
<td>0.000785</td>
</tr>
</tbody>
</table>

The total number of anions or cations present in a droplet of radius \( R \) that just meets the Rayleigh limit is given by

\[
N_\pm = \frac{4\pi R^3}{z_\pm} \left[ \frac{2t_\pm Q}{Q_e |Q|} \right] \sqrt{\frac{\epsilon_0 \sigma}{R^3}} \sqrt{\frac{\epsilon_0 \sigma}{R^3}} \tag{15}
\]

which follows from Eqs. (11) and (13). This equation reveals the total cation and anion content of the droplet but provides no information on the ways in which these ions are distributed within the droplet. The remainder of this article is directed towards determining these distributions.

3. Poisson–Boltzmann distribution theory applied to droplets

The field just outside a droplet is given by

\[
-\left( \frac{d\phi}{dr} \right)_{r=R^+} = \frac{Q}{4\pi \epsilon_0 R^2}\tag{16}
\]

according to Gauss’s law [8]. Here our interest is in the conditions just inside such a droplet, where the field is smaller than that given by Eq. (16) by a factor equal to the dielectric constant of water, so that

\[
-\left( \frac{d\phi}{dr} \right)_{r=R^+} = \frac{Q}{4\pi \epsilon R^2}\tag{17}
\]

where \( \phi \) now denotes the local electrical potential (V) within the droplet and \( \epsilon \) is the solution’s permittivity (close to the 6.854 × 10\(^{-10}\) F m\(^{-1}\) value for water at 298 K). Because only differences in potential are significant within the droplet, we shall adopt a potential scale that has its zero at the centre of the droplet. Gauss’s law also applies within the body of the droplet, permitting us to write

\[
\frac{d\phi}{dr} (r) = -\frac{Q(r)}{4\pi \epsilon \sigma^2}\tag{18}
\]

provided that \( 0 \leq r \leq R \), where \( Q(r) \) is the charge within a sphere of radius \( r \) centred at the drop’s centre.

Of course the charge in the droplet corresponds to a disparity between the numbers of cationic and anionic charges present. In this paper it is assumed that the solution contains only one cationic species, of charge number \( z_+ \), and a single anionic species of charge number \( z_- \) (which will invariably be a negative dimensionless integer). Let \( n_+ (r) \), \( n_- (r) \) and \( q (r) \) denote the cation number density \( (\text{m}^{-3}) \), the anion number density and the volumetric charge density \( (\text{C m}^{-3}) \) in the solution at a distance \( r \) from the drop’s centre. These three quantities are interrelated by

\[\]
\[ Q_d \left[ z_+ n_+ (r) + z_- n_- (r) \right] = q(r) \]  (19)

According to Boltzmann’s law, the twin equations
\[ n_\pm (r) = n^0_\pm \exp \{- z_\pm f \phi (r) \} \]  (20)

hold, where a superscript zero denotes conditions at \( r = 0 \) and \( f \) represents the Boltzmann voltage factor \((Q_e/k_B T = 38.9215 \text{ V}^{-1} \text{ at } 298 \text{ K})\). The last two equations combine into
\[ q(r) = Q_d \left[ z_+ n^0_+ \exp \{- z_+ f \phi (r) \} \right. \]
\[ \left. + z_- n^0_- \exp \{- z_- f \phi (r) \} \right] \]  (21)

which, through constants, relates the charge density at any point in the solution to the electrical potential there. Though the charge density at the droplet’s centre will be small, there is no reason to assume it to be zero and therefore we cannot equate \( z_+ n^0_+ \) to \(-z_- n^0_-\) as in the boundary conditions for the corresponding Poisson–Boltzmann treatments of ionic distributions in the Gouy–Chapman theory of double-layers [9] or surrounding each ion in the Debye–Hückel theory [10] of ionic activity coefficients. In this respect, the present problem resembles that solved by Farina and Oldham [11] for an electrolyte solution filling the narrow gap between two electrodes.

Poisson’s equation in spherical polar coordinates is
\[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d \phi}{dr} \right) = -\frac{\epsilon q(r)}{\epsilon} \]  (22)

when there is complete angular symmetry. On incorporation of Eq. (21), the Poisson formula, which holds in \( 0 \leq r \leq R \), becomes
\[ \frac{d}{dr} \left( r^2 \frac{d \phi}{dr} \right) = -\frac{Q}{\epsilon} \left[ z_+ n^0_+ \exp \{- z_+ f \phi \} \right. \]
\[ \left. + z_- n^0_- \exp \{- z_- f \phi \} \right] \]  (23)

This is the Poisson–Boltzmann equation that is to be solved, subject to two boundary conditions. One of these derives from Gauss’s law, Eq. (17), and is
\[ \frac{d \phi}{dr} = -\frac{Q}{4\pi \epsilon R^2} \quad \text{at} \quad r = R \]  (24)

A second boundary condition recognizes that, to avoid a discontinuity there, the electric field must vanish at the droplet’s centre and therefore
\[ \frac{d \phi}{dr} = 0 \quad \text{at} \quad r = 0 \]  (25)

We also know that the value of the dimensionless potential at \( r = 0 \) is
\[ \phi = 0 \quad \text{at} \quad r = 0 \]  (26)

which is a consequence of our choice of the origin of the potential scale. In practice, Eqs. (26) and (25) are the boundary conditions that we enforce. Condition (24) will serve as a means of checking the validity of our results.

The solution of Eq. (23) is impeded by the fact that the number densities \( n^0_+ \) and \( n^0_- \) at the droplet’s centre are not known a priori. To circumvent this difficulty, we regard \( Q \) as initially unknown and adopt wisely chosen putative values of \( n^0_+ \) and \( n^0_- \) from which the corresponding charge is found by the methods soon to be described. Then \( n^0_+ \) and \( n^0_- \) are iteratively adjusted until the sought \( Q \) is recovered. In all the cases that we report here, the charge that was sought was the largest positive charge that satisfied the Rayleigh criterion, namely
\[ Q = 8\pi \sqrt{a_0 \sigma R^3} = (2.0066 \times 10^{-5} \text{ C m}^{-3/2}) R^{3/2} \]  (27)

Of course, our procedures can equally well generate the properties of droplets with charges less than the Rayleigh charge limit.

4. Series solution

The Poisson–Boltzmann relationship, Eq. (23), is a non-linear second-order differential equation, a class to which analytical solutions seldom exist. Nevertheless, a power series solution, that also meets conditions (26) and (25), can be found by standard procedures. The solution makes use of the definitions
\[ a_i = \frac{z^{\ell+1} n^0_+ + z^{\ell+1} n^0_-}{\ell!} \quad \text{for} \quad i = 0, 1, 2, \ldots \]  (28)

and is of the form
\[ \phi = -\frac{1}{f} \sum_{k=1}^{\infty} B_k \left( \frac{Q}{f} r^2 \right)^k \]  (29)

where
\[ B_1 = \frac{a_0}{6} \quad B_2 = \frac{a_0 a_1}{120} \quad B_3 = \frac{a_0 a_1^2 + a_0^2 a_2}{5040} + \frac{a_0^3 a_3}{1512} \]
\[ B_4 = \frac{a_0 a_1^3}{362880} + \frac{31 a_0^2 a_1 a_2}{1088640} + \frac{a_0^4 a_3}{93312}, \text{ etc.} \]  (30)

It becomes increasingly tedious to calculate higher \( B \) coefficients and so this route ceases to be useful when \( \phi \) is large. When applicable, the series method may be used for calculating not only the electrical potential, via Eq. (29), but also the electric field strength,
\[ -\frac{d \phi}{dr} = \frac{2}{fr} \sum_{k=1}^{\infty} k B_k \left( \frac{Q}{f} \right)^k \]  (31)

the charge density via Poisson’s equation,
\[ q = Q_e \sum_{k=1}^{\infty} 2k(2k+1) B_k \left( \frac{Q}{f} r^2 \right)^k \]  (32)
and the charge contained up to \( r = r \), found by integration of Eq. (32),

\[
Q(r) = 4\pi \int_0^r r^2 q \, dr = \frac{8\pi e r}{f} \sum_{k=1}^{\infty} k B_k \left( \frac{Q_e f r^2}{e} \right)^k
\]  

(33)

Notice that the Gauss relationship (18) results from division of Eq. (31) by Eq. (33).

Though this series solution easily provides values of all the electrical properties of the droplet interior at all values of \( r \) for which \( \phi \) is small, it less easily yields information about the concentricative properties. In particular, the individual cationic and anionic number densities \( n_+ \) and \( n_- \) are not directly accessible as analytical expressions, even when the potential is small. Nevertheless, this information is available indirectly. Notice from the twin equations (20) that, for any value of \( r \)

\[
\left( \frac{n_+}{n_-} \right)^{z-} = \left( \frac{n_0}{n_-} \right)_{\phi
+}^{z-} \]

(34)

and that from Eq. (14)

\[
z_+ n_+ + z_- n_- = \frac{q}{Q_e}
\]

(35)

These are two simultaneous equations from which either \( n_+ \) or \( n_- \) may be eliminated. Taking the latter option, one may arrive at

\[
(n_+)^{m+1} - \left( \frac{q}{z_+ Q_e} \right) n_+ - m(n_0)^m n_- = 0 \quad \text{where}
\]

\[
m = - \frac{z_-}{z_+}
\]

(36)

This will be a quadratic equation in \( n_+ \), for electrolytes such as HCl or MgSO₄, or a cubic equation for such salts as Ca(NO₃)₂ or K₃C₆H₅O₇, and it will be readily solvable in all cases. By this route, Eq. (32) provides access to values of the ionic number densities at all values of \( r \) for which \( \phi \) is sufficiently small.

For droplets from which anions are completely absent, so that Eqs. (12) and (14) hold, the series solution (Eqs. (27)–(29)) simplifies and may be written

\[
x = x_0 \sinh \left( \frac{z_+ f \phi}{6e} \frac{r^2}{2L} \right)
\]

(37)

This slowly convergent series can be used to calculate the potential profile in the droplet, provided that \( x \) is not too large. Because \( z_+^2 n_+^0 / 2L \) is, in this case, equal to the ionic strength \( \mu^0 \) at the droplet’s centre, the dimensionless distance variable \( x \) is related to the Debye length [12]

\[
\lambda_{\text{Debye}}^0 = \sqrt{\varepsilon / 2Ff^2 \mu^0}
\]

establishing contact with classical Poisson–Boltzmann theory. In fact, \( 6x = (r / \lambda_{\text{Debye}}^0)^2 \).

5. Simulative solution

In the manner of an onion, let many concentric shells be created within the droplet, each of thickness \( \delta \), with the \( j \)th shell being bounded by spheres of radii \( r = (j - \frac{1}{2}) \delta \) and \( r = (j + \frac{1}{2}) \delta \). The zeroth ‘shell’ is a sphere of radius \( r = \frac{1}{2} \delta \), while the outermost shell has an outer radius of \( r = (J + \frac{1}{2}) \delta = R \), with \( J \) being an integer large enough that increasing it further makes no significant difference to the results. For the most part, we chose \( \delta \) close to 0.31073 nm, because \( \delta^3 \) is then 3.0003 \times 10^{-29} \) m³, equal to the molecular volume, \( V_{\text{H₂O}} \) of H₂O in liquid water. With this value of \( \delta \), the zeroth ‘shell’ is just a single water molecule and proceeding from \( (j - \frac{1}{2}) \delta \) to \( (j + \frac{1}{2}) \delta \) corresponds to adding a complete shell of water molecules.

Using the concentration definitions (again, in equivalents per unit volume)

\[
C^0 = \frac{z_+ n_0 + z_- n_-}{2L} \quad \text{and} \quad \Delta C^0 = \frac{z_+ n_0 + z_- n_-}{L}
\]

(38)

to replace the number densities \( n_+^0 \) and \( n_-^0 \), Eq. (23) may be redrafted as

\[
\frac{d}{dr} \left( r^2 \frac{d\phi}{dr} \right) = - \frac{Q_e L r^2}{e} \left[ C^0 h \{ \phi \} + \frac{\Delta C^0}{2} H \{ \phi \} \right]
\]

(39)

where we have adopted the abbreviations³

\[
h \{ \phi \} = \cosh \{ z_+ f \phi \} - \cosh \{ z_- f \phi \} - \sinh \{ z_+ f \phi \}
\]

\[
+ \sinh \{ z_- f \phi \}
\]

(40)

and⁴

\[
H \{ \phi \} = \cosh \{ z_+ f \phi \} + \cosh \{ z_- f \phi \} - \sinh \{ z_+ f \phi \}
\]

\[
- \sinh \{ z_- f \phi \}
\]

(41)

If we let \( \phi_j \) denote the value of the potential \( \phi(r) \) at \( r = j \delta \), then formula (39) may be discretized first to

³ When \( \phi \) is small, the two hyperbolic cosine terms are both close to unity and considerable numerical cancellation occurs in differencing them in Eq. (40). If the order of terms shown is not respected, serious loss of arithmetic precision may result. For similar reasons, do not be tempted to replace the hyperbolic terms in Eqs. (40) and (41) by their exponential equivalents.

⁴ When \( \phi \) is very small, we use the approximation \( \sinh \{ x \} = x \) in evaluating Eqs. (40) and (41) because otherwise there is too much loss of arithmetic precision in calculating the hyperbolic sine from \( \exp \{ x \} - \exp \{ -x \} \}/2 \).
\[
\left( r^2 \frac{d\phi}{dr} \right)_{r = (j + 1/2)\delta} - \left( r^2 \frac{d\phi}{dr} \right)_{r = (j - 1/2)\delta} = \frac{-Fr^2}{\epsilon} \left[ \overline{C}_0 h \{\phi_j\} + \frac{\Delta C_0}{2} H \{\phi_j\} \right] \tag{42}
\]

Then, by making the approximation that

\[
r^2 \frac{d\phi}{dr} = (j + \frac{1}{2})^2 \theta_{j+1} - \phi_j \delta \tag{43}
\]

and using a similar formula appropriate to \( r = (j - \frac{1}{2})\delta \), one arrives at

\[
(j + \frac{1}{2})^2 \theta_{j+1} - \phi_j - (j - \frac{1}{2})^2 \theta_j - \phi_{j-1} = \frac{-j^2\delta^2}{\epsilon} \left[ \overline{C}_0 h \{\phi_j\} + \frac{\Delta C_0}{2} H \{\phi_j\} \right] + (2j + \frac{1}{2})\phi_j - (j - \frac{1}{2})^2 \phi_{j-1},
\]

from which

\[
\phi_{j+1} = \frac{-j^2\delta^2}{\epsilon} \overline{C}_0 h \{\phi_j\} + \frac{\Delta C_0}{2} H \{\phi_j\} + (2j + \frac{1}{2})\phi_j - (j - \frac{1}{2})^2 \phi_{j-1},
\]

may be obtained on rearrangement.

Eq. (45) is a recursion formula which permits the potential midway through each shell to be determined from the two previous values. Starting with \( \phi_0 = 0 \) and the value

\[
\phi_1 = \frac{-F\Delta C_0\delta^2}{6\epsilon} \left( 1 + \frac{F J \delta^2}{40\epsilon} \right) [2(z_+ + z_-)\overline{C}_0 + (z_+ - z_-)\Delta C_0]\tag{46}
\]

derived from the first two terms in Eq. (29) with \( r = \delta \), successive values in a long sequence of \( \phi_j \) potentials may be evaluated by repeatedly implementing Eq. (45) until \( j = J \) is reached.

Of greater interest than the values of \( \phi_j \) themselves are the difference terms

\[
D_{J+(1/2)\delta} = \frac{\phi_{j+1} - \phi_j}{\delta}
\]

(47)

together with values of the two running sums

\[
(N_+)(J+(1/2)\delta) = \frac{2\pi L(2\overline{C}_0 + \Delta C_0)\delta^3}{z_+} \left[ \frac{1}{24} + \sum_{j=1}^{J-1/2} (j^2 + \frac{1}{12}) \right. \exp \{-z_+ f\phi_j\},
\]

(48)

\[
(N_-)(J+(1/2)\delta) = \frac{2\pi L(2\overline{C}_0 - \Delta C_0)\delta^3}{z_-} \left[ \frac{1}{24} + \sum_{j=1}^{J-1/2} (j^2 + \frac{1}{12}) \right. \exp \{-z_- f\phi_j\}.
\]

(49)

This is because these three can provide excellent approximations to several important quantities at radial locations \( r = (j + \frac{1}{2})\delta \) and, in particular, at the surface of the droplet, where the radius \( r = (J + \frac{1}{2})\delta = R \). These quantities are: the potential gradient at the drop surface

\[
\left( \frac{d\phi}{dr} \right)_{r = R} \approx D_{J+(1/2)\delta}
\]

(50)

the total numbers of cations or anions within the droplet

\[
N_\pm = 4\pi \int_0^R r^2 n_\pm \, dr \approx (N_+)(J+(1/2)\delta)
\]

(51)

and the total charge within the spherical drop

\[
Q = 4\pi \int_0^R r^2 q \, dr \approx Q(\pm)(J+(1/2)\delta)
\]

(52)

Thus the simulative solution permits us to find the following local properties: the electrical potential, the electric field, the charge density and the number densities of the anions and cations, at all points in the droplet, including the drop surface. As well, we can find the total charge and how it is composed of anionic and cationic contributions.

It should be emphasized that the only approximations involved in the simulative solution are those implicit in Eq. (46) and those attendant on replacement of a continuous problem by its discrete equivalent. To be sure that neither of these approximations introduces a significant error, we applied a numerical test which consists of checking that Eq. (18) is obeyed. This implies

\[
\frac{-j^2\delta^2}{\epsilon} \overline{C}_0 h \{\phi_j\} + \frac{\Delta C_0}{2} H \{\phi_j\} + (2j + \frac{1}{2})\phi_j - (j - \frac{1}{2})^2 \phi_{j-1} = z_+(N_+)(J+(1/2)\delta) + z_-(N_-)(J+(1/2)\delta)
\]

(53)

where, in the initial step, expressions equivalent to Eqs. (50) and (52) were introduced.

6. Procedure and results

Because all the results that we present relate to a droplet that just meets the Rayleigh criterion, the choice of the drop radius \( R \) fixes the value of \( Q \). Therefore, the procedure that we adopted was to vary the value of \( \Delta C_0 \), for some round value of \( \overline{C}_0 \), until the
total charge according to the simulative solution matched the sought (Rayleigh) value of $Q$. In all cases, we checked that condition (53) was satisfied and, if not, we decreased the size of $\delta$ until concordance was achieved. This check was carried out for every $j$ value, but poor concordance for small values of $j$ was not a matter for concern. The simulation enabled us to find values of the potential $\phi$, the ionic concentrations $C_\pm$ and the charge density $q$, not only at the droplet’s surface but also at many points in the range $0 < r < R$. For each simulation we computed values of the total numbers $N_+$ of cations and $N_-$ of anions. We also determined the numbers of cations and anions located between $r = R$ and $r = R - \frac{V_{H_2O}}{3}$, which we interpret as the numbers of ions ‘at’ the droplet’s surface. As well, we calculated, from Eq. (9), the concentration $C$ that the aqueous feed solution needed to have in order to generate a droplet with the required properties, assuming equal anionic and cationic mobilities. Finally, the cationic enrichment was calculated. This is the percentage by which the number of cations in the charged droplet exceeds the number in a similar volume of feed solution. If the ionic mobilities are equal then the cationic enrichment equals the anionic denudation (the percentage by which the number of anions in the charged droplet is exceeded by the number in a similar volume of feed solution).

Fig. 2 shows an example of the potential profile for a droplet from which anions are absent. The results of the simulation are compared with the predictions of series (37). The close agreement lends support to both methods of analysis. The small discrepancy can be attributed to the use of only seven terms in the series.

All the results that we report are for positively charged droplets that meet the Rayleigh criterion and where the cation and anion have equal mobilities. Apart from in Fig. 5, the results reported are for $z_+ = 1$ and $z_- = -1$.

Concentration profiles are shown in Figs. 3–5. For two different droplet sizes, Figs. 3 and 4 show the effect of the concentration of the feed solution on the ionic concentration profiles. One of the curves in each figure relates to the special case in which anions are totally absent. Notice that, as expected, the concentration gradients are most pronounced in the outer regions of the drop, especially when the concentration is high. On the other hand, the denudation of the inner regions of the droplet is most pronounced at low concentrations. Fig. 5 shows that the effect of charge numbers is not very great, at least for the cases illustrated.
of electrolyte solution. We find that only a minority of the charge is actually located in the surface layer of the drop. For example, the data for a 0.1 μm droplet in Table 2 indicate that less than 10% of the total charge is to be found ‘on’ the surface. This percentage reflects only the electrical forces acting on the charges. It must be recognized that the environment of an ion on the surface differs from that of an ion surrounded by water molecules, leading to a chemical effect in addition to coulombic forces. With most simple ions, though not all, these chemical forces would tend to reduce still further the percentage of ions located on the surface.

Our treatment of ionic distribution within a liquid droplet is strictly analogous to that used by Debye and Hückel [13] in investigating the distribution of ions around a ‘central ion’ and, more particularly, that employed by Gouy [14] and Chapman [15] in their studies of ionic distributions adjacent to a planar interface. As such, it incorporates the deficiencies that exist in those theories. For example, our approach ignores the fact that the centres of ions cannot occupy a narrow region immediately adjacent to the drop’s surface. In the Gouy–Chapman theory this anomaly was corrected by Stern’s [16] postulate of an inaccessible dielectric layer. A deficiency in the Stern treatment, and equally in ours, is the failure to recognise that the cations and anions might have different radii, possibly as a result of hydration. It is well known, from the work of Frumkin and others [17], that ions of different charges often approach the solution | air interface to different distances. Finally, our treatment ascribes no chemical properties to the ions. At solution | metal interfaces chemical effects often lead to ‘specific adsorption’ of certain ions and chemical interactions likewise cause hydrophobic ions to accumulate at water | gas interfaces. It might be possible to accommodate some of these features within a treatment similar to the present

7. Discussion and summary

By solving the Poisson–Boltzmann problem we have uncovered the distribution of ions in a charged droplet

Table 2

Data for nine positively charged droplets that satisfy the Rayleigh criteria, when the ionic transport numbers are \( t_+ = 0.5 \)

<table>
<thead>
<tr>
<th>R [μm]</th>
<th>C [eq m(^{-3})]</th>
<th>( C^0 ) [eq m(^{-3})]</th>
<th>( ΔC^0 ) [eq m(^{-3})]</th>
<th>( N_{+, \text{total}} )</th>
<th>( N_{-, \text{total}} )</th>
<th>Cations at surface</th>
<th>Anions at surface</th>
<th>% Cation enrichment</th>
<th>( ϕ(R−)/mV )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>24.82</td>
<td>6.885</td>
<td>13.77</td>
<td>125</td>
<td>0</td>
<td>26</td>
<td>0</td>
<td>100</td>
<td>−58.0</td>
</tr>
<tr>
<td>0.106</td>
<td>100</td>
<td>100</td>
<td>0.1073</td>
<td>330</td>
<td>205</td>
<td>51</td>
<td>10</td>
<td>23</td>
<td>−23.6</td>
</tr>
<tr>
<td>502.6</td>
<td>500</td>
<td>1.280 × 10(^{-6})</td>
<td>1330</td>
<td>1205</td>
<td>153</td>
<td>85</td>
<td>5</td>
<td>10</td>
<td>−10.4</td>
</tr>
<tr>
<td>0.1</td>
<td>0.7849</td>
<td>0.08607</td>
<td>0.1721</td>
<td>3960</td>
<td>0</td>
<td>211</td>
<td>0</td>
<td>100</td>
<td>−102.9</td>
</tr>
<tr>
<td>1.446</td>
<td>1</td>
<td>3.212 × 10(^{-3})</td>
<td>5627</td>
<td>1667</td>
<td>237</td>
<td>2</td>
<td>54</td>
<td>60.6</td>
<td></td>
</tr>
<tr>
<td>5.238</td>
<td>5</td>
<td>3.721 × 10(^{-8})</td>
<td>15194</td>
<td>11234</td>
<td>373</td>
<td>37</td>
<td>15</td>
<td>31.0</td>
<td></td>
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<tr>
<td>1</td>
<td>0.02482</td>
<td>0.000937</td>
<td>1.874 × 10(^{-3})</td>
<td>125231</td>
<td>0</td>
<td>1885</td>
<td>0</td>
<td>100</td>
<td>−156.4</td>
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<tr>
<td>0.06572</td>
<td>0.05</td>
<td>7.816 × 10(^{-10})</td>
<td>228391</td>
<td>103161</td>
<td>2060</td>
<td>7</td>
<td>38</td>
<td>74.3</td>
<td></td>
</tr>
<tr>
<td>5.002</td>
<td>5</td>
<td>4.189 × 10(^{-9})</td>
<td>12681410</td>
<td>12556180</td>
<td>17062</td>
<td>8096</td>
<td>0.5</td>
<td>−10.3</td>
<td></td>
</tr>
</tbody>
</table>

The droplet has a radius \( R \) and is derived from an aqueous solution of 1:1 electrolyte with concentration \( C \). \( C^0 \) and \( ΔC^0 \) are the mean of the cationic and anionic concentrations at the centre of the drop and the difference between these two values. \( N_{+, \text{total}} \) give the total numbers of cations and anions; the difference between these two numbers is constant for any given droplet size. The sixth and seventh columns list the numbers of ions present in the outermost layer of water molecules. The percentage in the eighth column represents the cationic excess compared with that in the same volume of feed solution. The final column gives the electrical potential at the surface of the droplet with respect to its centre.
one, but only at the expense of added complexity and by introducing parameters that would destroy the generality of the results.

A result that may not always have been appreciated is that small, highly charged droplets can be totally devoid of the counterion. This situation arises with dilute feed solutions, in fact, only when $C < 25$ meq l$^{-1}$ for aqueous droplets of 0.01 μm radius. Nevertheless, in principle, the method can completely separate the anions and cations of a salt, say KCl(aq), the ultimate products being KOH(aq) + $\frac{1}{2}$H$_2$(g) at a negatively charged collector or HCl(aq) + $\frac{1}{2}$O$_2$(g) at an anodic collector.

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Appendix A

The role of surface charges in opposing surface tension is evident but the mechanism by which interior charges fill this role is less clear. However, any effect that interior charges have upon the surface must be due to the electric field to which they give rise there. Now, Gauss’s law tells us that the field strength at $r = R$ is independent of the distribution of spherically symmetrical interior charges and has the identical value, $Q/4\pi eR^2$, to that produced by the same charge $Q$ present at $r = R$.

Accordingly, we conclude that Rayleigh’s law holds irrespective of the location of the charges.

References