Additional Arguments for a Correction of the Debye-Hückel, Maxwell-Boltzmann Equations for Dilute Electrolyte Equilibria

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Abstract

Peter Debye and Erich Hückel had developed a theory for the ionic activity coefficients in dilute solutions of strong electrolytes some 95 years ago [1]. Their limiting law still stands and is confirmed as close to reality in many experiments. In a previous article [2], it is shown that these limiting activity coefficients arise because the electrical contribution in the electrochemical potential of ionic species is overestimated traditionally with a factor 2. The smaller value removes inconsistencies in the models and complies better with the basic electrostatic principles. In this article further evidence is given in support of this alternative description. As consequence the dilute activity coefficients become unity, e.g. are removed, which means that the electrochemical potential of ions in dilute solutions is expressed directly in concentration, instead of activity, which simplifies modelling in such dilute solutions.

Keywords

Debye-Hückel, Electrolyte, Activity Coefficients, Electrochemical Potential, Debye, Hückel

1. Introduction

The behavior of a strong electrolyte in the limit of high dilution is given by the formulae due to Debye and Hückel [1]. Modifications to the theories were discussed in 2009 [2]. This publication gives a discussion and additional information in support of the theory.

2. Thermodynamics

For the energy of a phase we can write:

$$dU = TdS - pdV + \sum \tilde{\mu}_i dn_i \qquad (1)$$

And for the Gibbs free energy:

$$dG = -SdT + Vdp + \sum \tilde{\mu}_i dn_i \qquad (2)$$

The free energy is constant in a closed system (all $dn_i \equiv 0$) kept at constant temperature and pressure, e.g. at constant intensive variables ($dT = 0$, $dp = 0$).

We integrate the energy at constant intensities of a phase and differentiate to retrieve the Gibbs-Duhem equations:

$$0 = SdT - Vdp + \sum n_i d\tilde{\mu}_i \qquad (3)$$

The thermodynamics require that for ionic equilibrium in electric fields the electrochemical potential (e.g. total free energy per mole of ion i).

$$\tilde{\mu}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}} \qquad (4)$$

is constant for each constituent, over the regions that are accessible for these charged particles, where

$$\tilde{\mu}_i = \mu_i^0 + RT \ln \gamma_i c_i + z_i F \phi_i \qquad (5)$$

Here γ_i is the activity coefficient, F the Faraday constant, c_i the concentration of ion i, z_i the charge of ion i, ϕ_i the total electric potential experienced by the ion i from the surrounding ions (ion cloud) and (if present) the externally applied electrical field, R the gas constant, and T the absolute temperature. Normally, for uncharged phases, we add the chemical components as neutral salts, but with a nonzero space charge that need not be the case. In chemical experiments we often assume that the space charge is still zero, and the charges accumulate on surfaces, with the counter charge nearby (polarized electrical double layers). If we express Equation (5) for one single ion: $\tilde{\mu}_i = \mu_i^0 + kT \ln \gamma_i c_i + z_i e \phi_i = \mu_i^0 + kT \ln \gamma_i c_i + q_i \phi_i$. The electrical work per ion is expressed as a product of ion charge times potential, where k is the Boltzmann constant and e the elementary positive charge.

The electrochemical potential often is expressed as Equation (5), containing an idealized chemical term $RT \ln c_i$ and an electrical term $z_i F \phi_i$. How we do the accounting of electrical and chemical energy in the electrochemical potential exactly is rather irrelevant, as it is only the total electrochemical potential that can be measured experimentally. Any deviation in the measurement from the defined idealized two model terms is accounted for via the activity coefficient γ_i:

$$\tilde{\mu}_i = \mu_i^0 + RT \ln c_i + z_i F \phi_i + RT \ln \gamma_i \qquad (6)$$

The chemical term and the electrical term are idealized contributions based on hypothetical "idealized" model systems. Any deviation from that ideal behavior for real systems goes into the last term on the right-hand side of Equation (6) containing the activity coefficient. If the idealized chemical and electrical term together describes reality well, then the activity coefficient γ_i is close to unity and the last term on the right-hand side of Equation (6) is only a small correction.

The chemical part is obviously based on the idealized system that obeys the Maxwell-Boltzmann distribution law. This equation has proven its merits in many chemical experiments involving mixtures of uncharged chemicals (e.g. ideal mixing behavior).

The electrical part $z_i e \phi_I = q_i \phi_i$ per ion is obviously based on the notion that electrical work can be expressed as a differential electrical work contribution $dW_e = \phi dq$ for a test charge dq brought to a potential ϕ, or as $dW_e = qd\phi$ where we let a charge q charge travel through a potential difference $d\phi$. Since $dW_e = F_e dx$ we may also write $F_e = d\phi/dx = E$, where E is the electrical field strength in direction x, such that the electrical force is $F_e = qE$, which is equivalent to $dW_e = qd\phi$.

The question is now simply: Are these idealized model contributions for the chemical and electrical contribution chosen the best ones, e.g. do they lead to activity coefficients that are close to unity, so that the last term in the right-hand side of Equation (6) is only a small correction?

The activity coefficients can be obtained experimentally by all kind of experiments. Notably the potential measurements in concentration cells without transfer can be made very accurate in determining the free energy and hence in determining the value of the activity coefficients. Thus, we can check our model terms by independent experiments and verify how accurate our idealized models are. If the activity coefficients appear close to unity, our chosen two models for respectively the chemical interaction and the electrical interaction are obeyed closely, or we are just lucky in the fact that the errors in the models compensate each other and cancel out.

We can also pose the two model contributions and try to set up an extra model for the expected "idealized" deviations from the reality and calculate model predictions for the activity coefficients. This is essentially the route taken by Debye and Hückel. They model the deviations from the idealized terms as given by the Coulombic interaction energy calculated from the presence of the ion cloud of a smeared out rotationally symmetric opposing charge surrounding each ion in solution. Experiments indicate that their model predictions are accurate in the low concentration range for aqueous mixtures of strong electrolytes, because in practice the measured activity coefficients follow the predicted trends at lower concentrations for the aqueous mixes of these strong electrolytes.

3. Debye-Hückel Model

The Debye-Hückel model represents ions as idealized point charges that have an electrical interaction as described by Coulombs law as captured in the Poisson equation. The ions distribute according to a Maxwell-Boltzmann distribution. This is the case both in the limiting law and in the extended equations. In the extended equations the point charges have a finite size.

There are local concentration variations for the ions as consequence of their charge: There is a higher probability to find a charge of opposite sign (that is at-

tracted) than of the same sign (that repel each other) near a particular charge. The interactions are calculated by assuming that the charge of counter ions average out to a smeared out rotationally-symmetric space charge or ion cloud that interacts with the central ion of exactly the opposite charge. Many of the inherent assumptions are touched upon in [3] [4] [5]. Ref. [4] also contains an introduction to the mean spherical approximation (MSA) theory.

According to the limiting law of Debye and Hückel:

$$RT \ln \gamma_i^{DH} = -\frac{z_i^2 eF\kappa}{8\pi\varepsilon} \tag{7}$$

or according to the extended equations of Debye-Hückel:

$$RT \ln \gamma_i^{DH} = -\frac{z_i^2 eF}{8\pi\varepsilon} \frac{\kappa}{1+\kappa a} \tag{8}$$

where e the elementary charge, ε the dielectric constant, a is the distance of closest approach of the ions and κ reciprocal of classic Debye length with

$$\kappa^2 = \frac{2F^2}{\varepsilon RT}\rho I \tag{9}$$

where I the ionic strength in molal units and ρ the density of the liquid. These model values for the activity coefficients have been shown many times to be accurate in the lower concentration range, where long-range charge-charge interactions, e.g. Coulombs interactions, dominate.

According to that same model we calculate the potential from the surrounding ion cloud within the limiting law as

$$\phi_i^{DH} = \frac{-z_i e\kappa}{4\pi\varepsilon} \tag{10}$$

or within the extended law as

$$\phi_i^{DH}(r=a) = \frac{-z_i e}{4\pi\varepsilon} \frac{\kappa}{1+\kappa a} \tag{11}$$

Hence, for both the limiting law and the extended law of Debye-Hückel theory, we may simply write:

$$RT \ln \gamma_i^{DH} = \frac{1}{2} z_i F \phi_i^{DH} \tag{12}$$

Apparently: we may write something like:

$$\tilde{\mu}_i = \mu_i^0 + RT \ln c_i + \frac{1}{2} z_i F \phi_i (\text{ion cloud}) + z_i F \phi_i (\text{external}) \tag{13}$$

In case of neutral salt solutions, when the external field is zero, we may write.

$$\tilde{\mu}_i = \mu_i^0 + RT \ln c_i + \frac{1}{2} z_i F \phi_i (\text{ion cloud}) \tag{14}$$

In that case we write for a completely dissociated 1-1 electrolyte at concentration c, without external potential, for the +ion:

$$\tilde{\mu}_+ = \mu_+^0 + RT \ln \gamma_+ c_+ = \mu_+^0 + RT \ln c_+ + \frac{1}{2} z_+ F \phi_+ (\text{ion cloud}) \tag{15}$$

And for the −ion:

$$\tilde{\mu}_- = \mu_-^0 + RT\ln\gamma_- c_- = \mu_-^0 + RT\ln c_- + \frac{1}{2}z_- F\phi_- \text{ (ion cloud)} \tag{16}$$

or for the total salt $c = c_+ = c_-$:

$$\mu_{salt} = \tilde{\mu}_+ + \tilde{\mu}_- = \mu_{salt}^0 + RT\ln\gamma_+ c_+ + RT\ln\gamma_- c_- = \mu_{salt}^0 + 2RT\ln\gamma_\pm c \tag{17}$$

where within the DH approximation the values for $\gamma_\pm = \gamma_+ = \gamma_-$ are equal and given by Equations (7)-(9). This equation has many times been proven a good approximation for the activity coefficients for aqueous electrolyte solutions in the lower concentration range. So, we can interpret the ion/cloud interaction in a neutral electrolyte as a chemical interaction Equation (17), e.g. expressed as activity coefficients, or an electrical interaction from the micro potentials as given by Equations (15) and (16).

Similar, but more complicated, equations result for the more general n-m electrolytes and their mixes, which are also good approximations in the lower concentration range, as shown by the independent experimental verification.

Now the dilemma is that Equation (13) shows that an ion in the classical theory responds differently to the potential from the ion cloud (micro potential) than to an external applied field (macro potential). It is strange that an ion can feel the difference between an externally applied electrical field and a local electrical field from surrounding ions. The response to the ion cloud is reasonably quantified in many independent experiments to determine mean ionic activity coefficients for mixtures of salts at low concentrations. The response to external fields are more difficult to measure as the c_+ and the c_- concentrations will become different and single ionic activity coefficients cannot be assessed in isolation.

The only suggestion I do in the article in JCIS is to assume that the factor ½ might be more general than only for the ion cloud in the DH theory. I show that if we redefine the electrochemical potential as

$$\tilde{\mu}_i = \mu_i^0 + RT\ln c_i + \frac{1}{2}z_i F\phi_i \tag{18}$$

and thus assume a different model for the electrical interaction, and repeat the procedure of DH, we arrive at almost the same equations, $\tilde{\mu}_i = \mu_i^0 + RT\ln\gamma_i^{DH}c_i$, in the limiting law:

$$RT\ln\gamma_i^{DH} = -\frac{z_i^2 eF\kappa\sqrt{\frac{1}{2}}}{8\pi\varepsilon} \tag{19}$$

or according to the extended equations

$$RT\ln\gamma_i^{DH} = -\frac{z_i^2 eF}{8\pi\varepsilon}\frac{\kappa\sqrt{\frac{1}{2}}}{1+\kappa a\sqrt{\frac{1}{2}}} \tag{20}$$

which can be equivalently, in both cases, again be written as:

$$\tilde{\mu}_i = \mu_i^0 + RT \ln c_i + \frac{1}{2} z_i F \phi_i \qquad (21)$$

This Equation (21) is a general equation where the potential ϕ_i is the total potential (both macro potential from an external field plus micro potential from the surrounding ion cloud). In this case the theory is internally consistent, because the starting Equation (18) is identical to the resulting Equation (21).

In case of an electrolyte without (external) macro potential we only have the micro potential from the surrounding ion cloud, and thus according to the extended DH model:

$$\frac{1}{2} z_i F \phi_i \left(\text{micropotential} \right) = RT \ln \gamma_i^{DH} = -\frac{z_i^2 eF}{8\pi\varepsilon} \frac{\kappa \sqrt{\frac{1}{2}}}{1 + \kappa a \sqrt{\frac{1}{2}}}$$

Thus, when we interpret the micro potential as a "chemical" interaction:

$$\tilde{\mu}_i = \mu_i^0 + RT \ln c_i - \frac{z_i^2 eF}{8\pi\varepsilon} \frac{\kappa \sqrt{\frac{1}{2}}}{1 + \kappa a \sqrt{\frac{1}{2}}}$$

or for a 1-1 salt:

$$\mu_{salt} = \tilde{\mu}_+ + \tilde{\mu}_- = \mu_{salt}^0 + RT \ln \gamma_+ c_+ + RT \ln \gamma_- c_-$$

$$= \mu_{salt}^0 + 2RT \ln c - 2 \frac{z_i^2 eF}{8\pi\varepsilon} \frac{\kappa \sqrt{\frac{1}{2}}}{1 + \kappa a \sqrt{\frac{1}{2}}}$$

The advantage is that now the theory is internally consistent: the equation for the electrochemical potential of an ion that we start with is reproduced in the model calculation exactly.

In the experimental showcase discussed in JCIS article, is shown that this equation even fits slightly better than the original DH, which indicates that the differences in practice are small, but still in favor of the new theory. In fact, the equations are identical if we replace $\kappa' = \kappa\sqrt{1/2}$, e.g. the new theory leads to a similar exponential decay of the potential of the ions of the ion cloud, only with a different reciprocal Debye length κ'. The counter ions are effectively a factor $\sqrt{2}$ further out, since their electrical interaction energy is only half of that in the classical DH theory. So, all the DH trends remain valid (proportionality of $RT \ln \gamma_i$ with $\sqrt{c}$, similar trends of 1-1, 1-2, 1-3, or 2-3 electrolytes, the impact of ionic strength etcetera), except for a slight change in the values of the activity coefficients from the extra factor $\sqrt{1/2}$.

As already stated, the terms chosen for the chemical and electrical contribution in the electrochemical potential are chosen arbitrarily and cannot be measured independently. Any misfit goes into the activity coefficients. But we have shown that a definition

$$\tilde{\mu}_i = \mu_i^0 + RT \ln c_i + \frac{1}{2} z_i F \phi_i \qquad (22)$$

or per ion

$$\tilde{\mu}_i = \mu_i^0 + kT \ln c_i + \frac{1}{2} z_i e \phi_i$$

will deliver activity coefficients that are close to unity in the low concentration Coulombic region where normally the DH activity coefficients apply. Therefore, the electrical interaction term used here is probably closer to reality, at least for the micro potential from the ion cloud.

The rest of this note is going to show that in many cases the definition of electrical work according to the last term in the last two equations is indeed appropriate.

4. Electrical Energy

4.1. Capacitor

The most striking example is the energy of an electrical capacitance. According to elementary electrodynamics for a capacitance charged to total charge q:

$$U = \frac{1}{2} q \phi \qquad (23)$$

where ϕ the potential. For the capacitor the charge is proportional to the voltage, with proportionality factor the capacitance C, $q = C\phi$, or the energy for charging to q in infinitesimal steps dq or $d\phi$:

$$U = \int_0^\phi q \, d\phi = \int_0^q \phi \, dq = \int_0^q \frac{q}{C} \, dq = \frac{1}{2} \frac{q^2}{C} = \frac{1}{2} q \phi \qquad (24)$$

Here q is the charge and ϕ is the potential. So although for an infinitesimal step $dU = \phi \, dq$ or $q \, d\phi$, without the factor 1/2, the total energy has this factor 1/2. If we look at a tiny part dA of the total area A of the capacitance that represents a tiny fraction dq of the total charge q, we may write $dU = 1/2 \, \phi \, dq$, which can be the case of a single elementary charge and its counter charge subjected to a potential difference ϕ.

4.2. Electro-Capillarity

In the ideally-polarised electrical double layer we can make a diffuse space charge close to a metal surface (like Mercury or Silver) and create a double layer. In that case the system again behaves like a differential capacitor c, where for the free energy per unit area or interfacial tension:

$$\gamma - \gamma_z = -\iint_{\phi_z} c \, d\phi^2 \qquad (25)$$

e.g. the free energy has in first order a parabolic shape around the point of zero charge with $c = \partial q / \partial \phi = -\partial^2 \gamma / \partial \phi^2$, which shows that the charge is in first order proportional to the potential difference. This is in fact the only system where we can easily create a variable space charge and a variable macroscopic potential.

4.3. Linear Superposition Principle

We may arrive at proportionality between charge and potential very generally via the linear superposition principle of electrostatics, which states that we may generate the response of a system by simply imposing the responses of the individual parts: We can calculate the total potential by summing the voltage contributions of all individual charges. So, if we double a charge in a general system of charges, the potential of that charge at any spot of the system will double its value, which is a generalization of $q = C\phi$ for the capacitor. So, for any single charge or system of charges, we may write for the potential $q = a\phi$, or for the energy, when we let all charges grow from zero:

$$U = \int_0^q \phi \, \mathrm{d}q = \int_0^q \frac{q}{\alpha} \, \mathrm{d}q = \frac{1}{2}\frac{q^2}{\alpha} = \frac{1}{2}q\phi$$

This is a very general equation based on the peculiarities of the Coulomb law that allows us to obey and apply the linear superposition principle.

It is obvious that for the electrical energy we may state the electrical contribution as the differential term $\phi\mathrm{d}q$ or as the more integrated contribution $1/2q\phi$. In the first definition $\phi\mathrm{d}q$ you assume that you use an infinitely small test charge to probe the potential, such that the test charge does not change the potential. In the last definition $1/2q\phi$ you allow both the potential and the charge to be finite and neither of them infinitesimally small, and simply calculate the total energy exactly, even if it involves only one ion extra brought in contact with a system of charges. In the electrochemical potential both the charge and the potential are not infinitesimally small, and hence that last definition is therefore more appropriate and closer to reality for any real system, even for a single ion and its counter charge in the surrounding ion cloud.

If we now return to Equation (13) we see that we apparently may apply for the very small local field of order of one elementary test charge and a voltage of a few mV (as in the ion cloud in not too high concentrations, say up to 0.1 M) we must apply the integrated equation $1/2q\phi$ for the electrical energy to be accurate, but for the external potential, for which both charge and potential can be large, involving large numbers of ions, in order of Avogadro's number, and large potentials (Volts), we still resort to the differential form, $\phi\mathrm{d}q$, which we somehow miraculously integrate to ϕq, e.g. $zF\phi$, as if we can assemble the charges by summing many small test charges without affecting the field. Is that not weird? I would expect that if the small local system of the ion cloud and a large system like a capacitor all give $1/2q\phi$, we should also expect such a response in the electrochemical potential, e.g. $1/2z_iF\phi$, which is in fact just a similar system.

4.4. Assembly of Charges

Let us assemble a collection of point charges into a dielectric, or into a finite free space, from originally infinitely apart, e.g. initially without any energy of mutual interaction [6]. For bringing a first charge in a (zero) field from infinity we spend no electrical work:

$$W_1 = 0 \tag{26}$$

For bringing in a second charge we spend:

$$W_2 = q_2 \phi_1(r_2) = q_1 \phi_2(r_1) \tag{27}$$

where $\phi_1(r_2)$ potential of ion 1 at the position of ion 2 and $\phi_2(r_1)$ potential of ion 2 at the position of ion 1. Per ion we have spent for two charges $1/2 q\phi$.

For bringing in the third charge:

$$W_3 = q_3 \left[\phi_1(r_3) + \phi_2(r_3) \right] \tag{28}$$

For the three charges we have spent in total
$W = W_2 + W_3 = q_2 \phi_1(r_2) + q_3 \left[\phi_1(r_3) + \phi_2(r_3) \right]$, or again $1/2 q\phi$ per charge.

For the transport of the n-th charge

$$W_n = q_n \left[\phi_1(r_n) + \phi_2(r_n) + \cdots + \phi_{n-1}(r_n) \right] \tag{29}$$

The total electrical free energy is given by the sum of all W_i:

$$W = \sum_{i=2}^{N} W_i = \sum_{i=2}^{N} q_i \sum_{k=1}^{i-1} \phi_k(r_i) \tag{30}$$

We can now replace the potentials by their explicit expressions:

$$\phi_k(r_i) = \frac{q_k}{4\pi\varepsilon |r_i - r_k|} \tag{31}$$

then such energy can be expressed as

$$W = \sum_{i=2}^{N} \sum_{k=1}^{i-1} \frac{q_i q_k}{4\pi\varepsilon |r_i - r_k|} = \frac{1}{2} \sum_{i}^{N} q_i \sum_{k \neq i}^{N} \frac{q_k}{4\pi\varepsilon |r_i - r_k|} \tag{32}$$

or

$$W = \frac{1}{2} \sum_{i}^{N} q_i \phi(r_i) \tag{33}$$

where $\phi(r_i)$ the total potential at the position of charge i of all surrounding charges. In summing over all particles would count every interaction twice, hence the factor $1/2$ in front of the second summation in Equation (32), which is the same as saying that the pair interaction energy must be equally divided over each of the two ions involved.

So, if we want to calculate the electrical energy of a particular ion in a sea of positive and negative ions, we may simply hypothetically freeze the system and calculate the potential ϕ at the spot of the ion from all the other ions. The electrical energy per ion is

$$\Delta W = \frac{W}{N} = \frac{1}{2} \frac{\sum_{i}^{N} q_i \phi(r_i)}{N} = \left(\frac{1}{2} q\phi \right)_{averaged} \tag{34}$$

Here we see that for any general assembly of charges, we may calculate the total electrical energy as a contribution of order $1/2 q\phi$ for the ion charge introduced in the field of the other ions. Here it is immaterial whether the charges are ideal point charges or have a finite volume, or are dipoles, if they are separated in

space, such that they do not occupy the same volume element. The contributions of ions and (water) dipoles simply add together. Often, we treat the water as a continuous dielectric with a dielectric constant, which is probably most of the time a good approximation. The presence of the dielectric modifies the field, and thus the value of the potential at the spot of each ion.

In an electrolyte the positive and negative charges almost cancel each other in the effective electrical potential, except for the ion cloud of opposite sign around the ion, in double layers, and in the case that an effective nonzero space charge is present from unbalance in positive and negative charges.

Here we must realize that Equation (33) is <u>exact for the electrical work</u> needed to assemble any physical system of "point" charges, irrespective of the size of the individual charges and irrespective of the size of the ultimate resulting potentials, and independent of the path used to create that assembly: We can build up the field by assembling the charges from infinite distances apart, or let all charges grow from zero to their value while they are present at the right spot, or any other assembly process that is done at constant pressure and temperature. We only must require that the ions cannot occupy the same spot at the same time due to their finite size, as potentials would than explode to infinity. But that is a physically realistic assumption, even for electrons in a metal (in the classical electrostatic limit).

If $\frac{1}{2}q\phi$ is the perfect answer for the electrical Coulombic work needed to introduce one ion into a sea of other ions with effectively the opposite charge of the ion introduced, fully in line with the linear superposition principle of electrodynamics, why is that then not taken as the most perfect measure of the electrical energy term in the electrochemical potential, which is apparently traditionally taken qϕ, thus twice that value?

4.5. Cyclotron

In the cyclotron the energy gain per revolution is approximately $q\Delta\phi$ for each cycle of a charge q, where $\Delta\phi$ the imposed electrical potential difference in the cyclotron. In this formula $q\Delta\phi$ the electrical field is assumed so strong that a single or a few particles with charges q in the beam do not matter, e.g. do not modify the strength of the imposed electrical field.

But if you look closely, the particles in the beam must interfere with the electrical field: They will modify the electrical field slightly by their presence via their reaction (imaging) forces. The total field therefore will depend on the presence of these particles. Only when there is no particle at all, $q\Delta\phi$, with $\Delta\phi$ the undisturbed electrical potential difference, is exactly right.

I am convinced that when particles are moving in the magnetic & electrical fields in the cyclotron, the fields are slightly, but significantly, modified. If two particles approach each other, the front one will accelerate and the rear one will lose speed. Moreover, the particles will interact with the magnets and charges that will adjust, although these forces will be small. Many charged particles build

up the field and therefore the few charges in the beam give only a slight interference of the effective field.

I am sure that when you try to find an exact solution, you would have to comply with $W = \dfrac{1}{2}\sum_{i}^{N} q_i \phi(r_i)$ exactly at any instant, where ϕ is the field at the position of particle i of all the charged particles that are building the field.

In this case $q\Delta\phi$ for a single particle is a simplifying mathematical approximation assuming that the charge of the particle is assumed infinitesimally small and does not change the potential difference $\Delta\phi$.

The same argument is traditionally used in the reaction field of a single ion: but that cannot be the case: The ion charge and the electrical reaction field of the surrounding ions are in their mutual effect of the same order of magnitude, and are fully building each other. Hence, we need to take the full energy equation including the factor 1/2.

4.6. Modelling the Electrical Interaction Term

The discussion above clearly shows that if we define according to Equation (5) the electrical part of the electrochemical potential per ion as

$$\Delta\tilde{\mu}_i \left(\text{electrical}\right) = \frac{+z_i F \phi_i}{N_A} = q_i \phi_i \tag{35}$$

that we are overestimating the electrical contribution with a factor 2 for every possible assembly of charges, while a contribution per ion:

$$\Delta\tilde{\mu}_i \left(\text{electrical}\right) = \frac{+\frac{1}{2} z_i F \phi_i}{N_A} = \frac{1}{2} q_i \phi_i \tag{36}$$

is right on spot for any possible configuration of any number of interacting ionic charges at any spatial configuration, notably including the case where we add one simple ion to a solution of very many ions, whose effective charge was just the opposite of the last ion added.

So, in the JCIS article I am not disputing the differential electrical work term $\mathrm{d}W = \phi\,\mathrm{d}q$ as appears in many fundamental equations for the work associated with introducing an infinitesimal test charge in an existing electrical field ϕ, but I show that the applicability of DH theory has indirectly proven us that the electrical work in the diffuse ion cloud of even a single ion can be more accurately be expressed as the more integrated formula $W = 1/2\, q\phi$.

And then I suggested that if such a model is appropriate for the small field of the ion cloud:

$$\tilde{\mu}_i = \mu_i^0 + RT \ln c_i + \frac{1}{2} z_i F \phi_i \left(\text{ion cloud}\right), \tag{37}$$

we might generalize that to all electrical interactions for strong electrolytes:

$$\tilde{\mu}_i = \mu_i^0 + RT \ln \gamma_i c_i + \frac{1}{2} z_i F \phi_i \tag{38}$$

Here the electrical energy is not the differential form $dU = \phi dq$, but chosen the integrated form $U = 1/2\phi q$, which is expected from elementary electrodynamics to be exact for any general assembly of charges. I show in the JCIS article that this equation even fits slightly better, e.g. results in activity coefficients that are closer to unity in the particular case that is often referred to as a classical example that shows the success of the standard DH theory.

I want to stress here again that any model chosen for the chemical and the electrical term in the electrochemical potential can only show its merits by the value of the activity coefficients in the range where the model is applicable.

For the calculation of the electrical contribution in the electrochemical potential we need a thermodynamic average of the electrical interaction energy per ion, averaged over a large assemble of ions, and the question remains whether this is described by the differential form ϕdq or, as I suggest better, by the generalized average $1/2q\phi$ as given by Equation (34) that, according to classical electrodynamics is appropriate for the long-range Coulombic interaction of any assembly of charged particles of any size or of any distribution and fully in line with the Superposition Principle of Electrostatics.

Now that we have a better, and more generally applicable, model for the free energy associated with the Coulombic electrical ionic interactions of strong electrolytes, inherently fully in line with the Superposition Principle of Electrostatics, correct for any microscopic and/or any macroscopic configuration or assembly of charges, dipoles, etcetera, it would be foolish not to use that improved model in the expression of the electrochemical potential of ions.

4.7. Electrical Work in an Electrochemical Cell

I want to show next that the normal equations for potential differences of electrochemical cells remain valid, irrespective of the adapted equations of the electrochemical potential.

Let us reconsider the concentration cell

$$Cu'|Ag, AgCl|HCl(m') \ H_2(Pt) - H_2(Pt)|HCl(m)|AgCl, Ag|Cu \qquad (39)$$
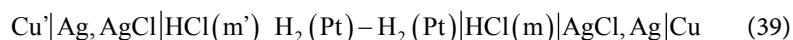
without transport with potential difference

$$emf = \phi_{right} - \phi_{left} = \Delta\phi \qquad (40)$$

With net reaction of 1 mole for 1 Faraday of charge ($n = 1$):

$$HCl(m') \rightarrow HCl(m) \qquad (41)$$

If an infinitely small electric charge dq is passed through the voltage drop emf in the external circuit, the system produces a quantity dW_{ext} of work:

$$dW_{ext} = emf \, dq \qquad (42)$$

(This equation is the integrated form of the familiar electrical formula: power = voltage × current).

If the cell operates reversibly at a given temperature and pressure, the external work is accompanied by a decrease dG in the free energy of the entire cell:

$$\mathrm{d}W_{ext} = -\mathrm{d}G \tag{43}$$

The free energy change is due to a reduction of dm moles of one reactant in the cathode and a simultaneous oxidation of dm moles of the other reactant in the anode. For one mole of reactants converted to products, the free energy change is ΔG, so for dm moles reacted:

$$\mathrm{d}G = \Delta G \mathrm{d}m \tag{44}$$

Combining the preceding three equations gives:

$$\Delta G \mathrm{d}m = -emf\, \mathrm{d}q \tag{45}$$

Let n be the number of electrons transferred for each atom reduced in the cathode and oxidized in the anode (for our reaction $n = 1$). The charge transferred for dm moles of overall reaction is:

$$\mathrm{d}q = eN_{AV}n\mathrm{d}m \tag{46}$$

where $e \cong 1.6 \times 10^{-19}$ Coulombs is the electronic charge, $N_{Av} \cong 6 \times 10^{23}$ is Avogadro's number and the product eN_{Av} is the charge of one mole of electrons. This product is called Faraday's constant, $F \cong 96500$ Coulombs/mole. Combining the above two equations yields the desired final result:

$$\Delta G = -n\left(eN_{AV}\right)emf = -nF \cdot emf \tag{47}$$

Here we have shown that for a reversible process, the electrode energy is $\Delta W = \Delta\phi\Delta q$ and not $\Delta W = 1/2\Delta\phi\Delta q$, because all the charge is travelling reversibly through the same potential difference $\Delta\phi$, that is assumed not to change during the charge transport: A good battery will keep its voltage nearly constant while a current is delivered.

A cell with a positive potential difference (right-left) indicates that the reaction inside is written qua direction as a spontaneous process ($\Delta G < 0$) towards further equilibrium: When the leads are connected through a high resistance the spontaneous reaction will create a small spontaneous current in the external circuit, e.g. the system acts as a charged battery.

We conclude that the new detailed equation for the electrochemical potential does not interfere with the equations derived for electrochemical cells.

4.8. Semi-Permeable Membrane

Let us now consider a classical example of the consequences of my modifications in the case of a semi-permeable membrane that only is permeable for the cation i of a 1-1 salt and not permeable for the anion j and not permeable for the solvent (water), in contact with two reservoirs, A (left) and B (right), of volume V containing the 1-1 salt at equal or different concentrations. This is a simple system.

Thermodynamic equilibrium requires constancy of the electrochemical potential of the cation:

$$\tilde{\mu}_i\left(A\right) = \tilde{\mu}_i\left(B\right) \tag{48}$$

Classically we would write

$$\mu_{0,i} + RT \ln a_i(A) + z_i F \phi_A = \mu_{0,i} + RT \ln a_i(B) + z_i F \phi_B \tag{49}$$

Or

$$RT \ln \frac{a_i(A)}{a_i(B)} = z_i F (\phi_B - \phi_A) = z_i F emf \tag{50}$$

This is as far as we get. Now we can make certain approximations to get some further, e.g. replace activities by concentrations and assume that the concentrations are close to the bulk concentrations of the salt, hence:

$$\frac{RT}{z_i F} \ln \frac{c(A)}{c(B)} \cong emf \tag{51}$$

This is essentially the classical approach.

But now let us look at this system more closely and bring some more physics in. If the concentrations in both cells are the same, the potentials are equal, and the space charge is zero. There might be some preferential adsorption of one of the ions, and therefore a polarized double layer on both sides, but the total charge on both sides will be zero. According to the superposition principle we may superimpose the adsorption and the membrane potential phenomena, hence we may forget for simplicity the polarized double-layer effect. In the solution the ions feel the micro potential of the surrounding ion cloud. We can also separate that effect via the superposition principle. Hence, we focus only on the macro potential from the presence of the membrane.

The electrical work for passage of charge through the membrane associated with the leakage of cations from the high to low concentration side is

$$dW_{\text{electrical}} = \phi dq_i \tag{52}$$

Here ϕ is the potential difference between the two sides of the membrane. Now we know that the charge build up is proportional to the voltage difference (as associated with increasing the concentration difference). In fact, here we recognize the behavior of an electrical capacitance again, $dq = Cd\phi$, which the membrane is, e.g. a charge separation in space, obeying the electrical linear superposition principle.

At equilibrium the chemical work should be equal to the electrical work, as the electrochemical potential is constant over the whole system:

$$dRT \ln a_i = -\phi dq_i \tag{53}$$

Hence, we may simply integrate the differential work to give:

$$RT \ln \frac{a_i(A)}{a_i(B)} = -\int \phi C d\phi = -\frac{1}{2} C \phi^2 = -\frac{1}{2} \phi q_i \tag{54}$$

Here we again recognize the Boltzmann law

$$\frac{a_i(A)}{a_i(B)} = \exp\left(\frac{-\frac{1}{2} \phi q_i}{RT} \right) \tag{55}$$

(The minus sign should be in accord with the chosen signs of potential difference and the sign of the charge). Here again the differential form in Equation (52) leads, because of the linear superposition principle, to an equilibrium Equation (54) that should contain a factor 1/2 in the integrated form. This I have not recognized in the membrane theories up till now, but would be required for a sound modelling of elementary membrane phenomena.

You might argue here that the capacitance might not be constant, e.g. it is a differential capacitance. But even then, the behavior is in first order quadratic in potential difference, and the higher order corrections set in at higher charges and potentials away from zero charge, very similar to the effects of the higher order corrections in the DH theory that are accounted for in the activity coefficients.

5. Extrapolation to Standard States at Infinite Dilution

In many experiments involving strong electrolytes we need to extrapolate the data to infinite dilution to get thermodynamic data for the electrolytes in the hypothetical infinite dilution reference state at unit activity (standard electrode potentials ϕ_o, reaction free energies ΔG_o, enthalpies, etcetera). In these extrapolations we traditionally employ the Debye-Hückel activity coefficients to extrapolate over the lower concentrations towards infinite dilution, as we had expected them to be essentially correct. Now I have shown that these traditional activity coefficients might be slightly in error. This might indicate that we must adapt the extrapolation procedure to incorporate the improved expressions for the activity coefficients, which might lead to slight, and even maybe sometimes even significant, changes in the extrapolated and published thermodynamic reference data for strong electrolytes and their electrode potentials. This is a fundamental result that might constitute a lot of work.

6. Summary

To summarize, we may state in general, fully in compliance with the definition of electrical work, that for two points of identical composition (two identical electrodes) per mole

$$\mathrm{d}\tilde{\mu}_i = z_i F \mathrm{d}\phi \tag{56}$$

or per ion:

$$\mathrm{d}\tilde{\mu}_i = z_i e \mathrm{d}\phi = q_i \mathrm{d}\phi \tag{57}$$

Normally the electrical work is defined as $\mathrm{d}W = \phi \mathrm{d}q$, where we bring an infinitesimal charge over a potential difference ϕ. In the last equation we have made the potential difference infinitesimally small. The equation is formally only correct for an infinitesimally small charge.

When we integrate this equation, e.g. create a measurable potential difference ϕ and a finite charge q_i, even for a single ion, the superposition principle requires that the potential and charge are proportional for any system that we create by

assembling a system of charges. It is immaterial whether the field creates the charges, or the charges create the field: They are building at the same time. This is the reason why for any significant (ionic) charge and any significant field ϕ:

$$\Delta\tilde{\mu}_i = \frac{1}{2}q_i\Delta\phi \tag{58}$$

This new formula with the factor ½ allows us to obey the linear superposition principle of elementary electrodynamics that states that for any assembly of charges in any configuration in space, the potential and charges are proportional. The consequences for the definition of the electrochemical potential are in practice small and absorbed in different values for the activity coefficients. But in this new way, obeying the superposition principle, we probably capture the elementary electrodynamics and physics better and thus make better and simpler models:

The fact that the activity coefficients are essentially closer to unity in the dilute Coulombic range, allows us to assume that the activity coefficients are equal to unity in that Coulombic range and hence replace in models the activity by simple concentration. This simplifies the models tremendously in further calculations as we may then state:

$$\tilde{\mu}_i = \mu_i^0 + RT\ln c_i + \frac{1}{2}z_i F\phi_i \tag{59}$$

where ϕ_i the total potential, containing (superimposed) contributions from micro and macro potentials and without activity coefficients, hence we have a simple fundamental equation linking concentration and total potential, that should accurately predict the behavior of electrolytes in an electrical field at low concentration in the range where Coulombic interactions dominate. This makes modelling work much easier.

Traditionally, we were caught in an iterative cycle: we need to express equations in activities that we do not know a priory. Hence in models and in numerical simulations/calculations we approximate the activities first by concentrations (thus forget about activity coefficients, e.g. approximate them by unity), evaluate the (now approximate) model expressed in concentrations and then calculate the local concentrations according to the model. We then calculate the (approximate) activity coefficients by some (DH) model to get a better (second) approximation for the local activities, and repeat the calculation with calculated activities, etcetera.

But in our new equation, the activity coefficients remain unity (are absent) in the lower concentration range where the Coulomb forces are dominant. The models are thus expressed directly in concentration, and need to be evaluated only once, with the same accuracy. This makes life easier, especially when the model requires the combination of external and local fields (like in the Gouy-Chapman theory for the ideally polarized electrode with an ideally polarized electrical double layer present [7], creating a field and a local difference in the local concentrations of anions and cations).

7. Discussion

As you see I offer an alternative formulation for the detailed modelling in the electrochemical potential of strong dilute electrolytes, which has some advantages, and is based on, to my opinion, sound physical principles.

You can <u>either</u> use the classic expression, which needs activity and activity coefficients even in the dilute range to correct for the less efficient modelling of the electrical interaction, separating the effect of the ion cloud out from the electrical interactions and bring them into the chemical energy, <u>or alternatively</u> use the new expression and define the chemical and electrical energies more efficiently, fully in line with the superposition principle and classical electrodynamics. In that last case the ion cloud is simply a part of the electrical field interaction as it should be, without the need to separate "macroscopic" and "microscopic" potentials, with different models. Such separate models are later difficult to unify in more elaborate systems like the electrical double layer, when both ion clouds and an effective space charge are present.

I have always found it difficult to unify the superposition principle of classical electrostatics, the classical energy equations in the electrostatic field, like those for capacitors, and the traditional definition of the electrical energy term in the electrochemical potential of ions. I hope that my alternative approach will help to resolve these issues and may give a better description, and a better basis for further modelling of electrochemical phenomena involving dilute strong electrolytes and electrical fields.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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