

Ion-Pairing: A Bygone Treatment of Electrolyte Solutions?

Lars Olow Simon Colbin,^{*,[a]} Yunqi Shao,^[a] and Reza Younesi^[a]

The field of battery research has advanced significantly in the past 50 years. Despite the importance of electrolyte solutions for these devices, the battery community's perception of this essential component arguably aligns more with the 19th century reasoning than the 20th centuries advancements. This paper traces the historical evolution of electrolyte theories, emphasizing the consequences of an overly ion-pairing-centric view, and the benefits of a more nuanced analysis. A quantitative example is provided. It will be shown that an association constant of

$K_a = 3.5$ can be obtained from conductivity measurements of sodium acetate in water. However, studying the activity coefficients of this electrolyte reveals that this association constant would result in an unreasonable scenario where the free ions behave as uncharged particles at low concentrations. The aim is to promote a nuanced perspective on electrolyte solutions within the battery community, while also providing a collection of reputable references for the interested readers further studies.

Introduction

About one hundred years ago, in 1923, Debye and Hückel unveiled their theory on ionic attractions,^[1] a concept still taught to undergraduate chemistry students today. This enduring theory finds practical application in comprehending the behavior of dilute electrolyte solutions, elucidating how both molar conductivity and electrochemical potential change with concentration. The theory builds on charged particles in a dielectric medium. In principle, the solvent's identity – be it aqueous or organic – should not affect the theory's applicability. However, the concentration where an electrolyte solution should be considered dilute can vary based on the solvent involved.

Before the advent of the ionic attraction theory, the prevailing understanding of electrochemical potential and molar conductivity suggested a more direct dependence on concentration, primarily influenced by the degree of ion dissociation.^[2–5] This traditional view, termed the “classical theory” by Debye and Hückel, faced criticism even before the introduction of their new theory.^[6–8] Lewis, as early as 1907, instead proposed the use of *activities*, as they are viewed today, and by 1921, Lewis and Randall demonstrated the limitations of relying solely on ion dissociation arguments.^[8,9]

Building on Lewis conventions, the use of activities to treat the energies within an electrolyte solution was further developed during the 20th century. This has served as a core for a variety of treatments of electrolyte solutions at any concen-

tration, ranging from rationalizing the driving force of electrochemical reactions^[10–13] to determining transference numbers.^[13–15] Historically, water has typically been the solvent system for both verifying the theory and determining parameters of electrolyte solutions. However, the thermodynamic treatment using activities would apply for any solvent system. Yet, the theoretical framework is usually constructed in a way that makes it hard to fully compare electrolyte solutions of different solvents.^[16,17]

Despite these past advances, it appears that the field of battery chemistry has reverted to a thinking reminiscent of the latter half of the 19th century. Now, two centuries later, ion-pairing has reemerged as a dominant factor in contemporary scientific reasoning. In fact, numerous contemporary publications tend to emphasize the influence of ion-pairing on ionic conductivity, while seemingly disregarding several advances of the 20th century.^[18–33] Moreover, modern literature occasionally even employ ion-pairing as a substitute for activity or to rationalize electrochemical reactions, though it is not as common as in conductivity arguments.

It is important to consider different scientific abstractions simultaneously, recognizing that the most useful model might not always offer the most precise predictions. While favoring simplicity for qualitative understanding can be beneficial, it becomes problematic if these simplifications distort our grasp of reality or impede further research. For instance, an exclusive focus on ion-pairing might lead to overlooking potentially sustainable materials due to too strict considerations of a solvent's dielectric constant or an anion's conjugate acid's pK_a-value. Achieving greener electrolyte solutions in battery chemistry is likely more attainable when exploring all viable options, rather than limiting considerations to a single viewpoint.

The historical evolution of the understanding of electrolyte solutions, particularly in terms of ion-pairing and activity, is here traced. An in-depth analysis is undertaken, focusing on ion-pairing concerning conductivity and activity, for an example solution – sodium acetate in water. The overarching aim is to discern whether the contemporary stance in battery research,

[a] L. O. S. Colbin, Y. Shao, R. Younesi
Department of Chemistry-Ångström Laboratory
Uppsala University
Box 538, SE-75121 Uppsala, Sweden
E-mail: Simon.colbin@kemi.uu.se

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seemingly neglecting the advancements of the past century, is justified. This investigation prompts the question: Do arguments centered around ion-pairing offer a more robust framework than discussions on the activity of an electrolyte solution?

Ion-Pairing

What is actually meant by ion-pairing is not always clear. The classical view from 19th century would be that an associated pair of ions is a different entity in the solution than that of the ions. The “association of ions” is thus a chemical reaction specified by its equilibrium constant and follows the so-called law of mass action, see Figure 1a. Mass action is likely a good approximation when the associated ions form a neutral molecule such as acetic acid. Moreover, a similar treatment of two oppositely charged ions in direct contact, or an aggregate of ions in contact, would also likely be acceptable, Figure 1b and c. However, what about ions that are simply close to each other, but not in direct contact?

In 1926, Bjerrum presented the idea that oppositely charged ions that are not in direct contact may still be counted as paired.^[34] Therein he presented an equation relating the dielectric constant, ϵ , to a distance, d , serving as the cut-off for when two ions should be counted as associated, Figure 1c. Bjerrum’s expression was soon to be criticized for inaccurate predictions of association constants.

Building on Bjerrum’s ideas, Fuoss would later suggest an alternative expression in 1934.^[35] Yet, throughout Fuoss’ career, he would present different views on what should be counted as ion pairs. In 1958, Fuoss presented a model insisting that only ions in direct contact should be counted as paired (Figure 1a–c). However, in 1967 he presented a conductivity analysis which suggested that solvent separated ion-pairs were included in the association constant (Figure 1f).^[36,37]

It is still unclear if non-contact ions should be considered as paired. Yet, counting non-contact ions as paired appears to have been further embraced towards the end of the 20th century.^[38] Now, in the 21st century, it is common to address ion-pairing in terms of solvent separated ion-pairs, solvent shared ion-pairs, contact ion-pairs, and aggregates of ions, Figure 1a–f.^[39–47] These concepts of non-contact ions are, however, arguably problematic in at least two aspects:

- (i) At a certain concentration, solvent separated and solvent shared ion-pairs should form by virtue of the number of solvent molecules available for coordination. For moderately large solvent molecules, e.g. triethyl phosphate, the formation of solvent shared ion-pairs should become unavoidable already at 1 mol/kg, since this solution would contain 5.5 solvent molecules per unit of monovalent electrolyte.
- (ii) The nomenclature implies that oppositely charged ions in relatively close proximity should be treated similarly to contact-pairs. However, these should behave distinctly different. For example, a true contact-pair would behave as a dipole in an electric field, whereas non-contact ion-pair are expected to conduct a current.

There is value in the contemporary mechanistic view enabled by the concept of solvent separated, solvent shared, and contact ion-pairing. The presence of non-contact ion-pairs would likely affect the properties of an electrolyte solution. Ions close together will both increase the electrostatic force between the ions, and also make short range interactions more relevant. Moreover, at a critical concentration, all solvent molecules would coordinate ions, resulting in the observation of either solvent separated, or solvent shared ion-pairs. This would likely mean that the dielectric medium between the ions would change drastically, thus changing how the different forces scale in the solution. Yet, these processes would likely not be well described by a chemical equilibrium, where some ions are effectively removed as conductors from the solution. However,

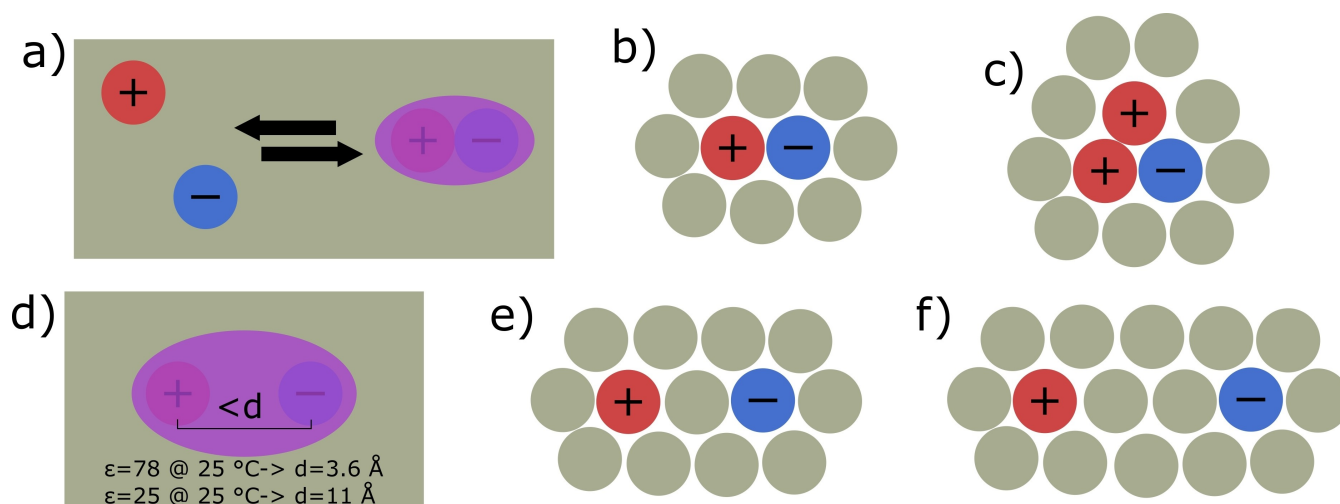


Figure 1. Different definitions of ion-pairs. a) A dielectric continuum where two ions are in equilibrium with a new particle formed by the of the two ions. b) A contact ion-pair surrounded by solvent molecules. c) An aggregate of contact ion-pairs surrounded by solvent molecules. d) A dielectric continuum where ions are considered one paired species if separated by a distance d . According to Bjerrum’s model, d is determined by temperature and dielectric constant. e) An ion-pair separated by shared solvent molecules, i.e. solvent shared ion-pair. f) An ion-pair separated by each ion’s solvent molecules.

the label, “ion-pairing” or “ion association” might indicate that this is the case. Regardless of the underlying phenomena, mass action could in principle be used to try to capture the effect of solvent separated, solvent shared, or contact ion-pairing. It is, however, questionable if this really is a good representation of what actually happens in the system, since non-contact pairs and some aggregates of ions are still expected to conduct current. Moreover, aggregates of ions with a net charge would have to be assigned its own mobility and equilibrium expression, introducing additional parameters that makes the initially simple concept of mass action vastly more complex. In essence, the expansion of the concept of ion pairing from considering a simple mass action equation can be summarized by one of Onsager’s alleged quotes about ion association:^[48]

“Bjerrum’s choice is good but we could vary it within reason. In a complete theory this would not matter; what we remove from one side of the ledger would be entered elsewhere with the same effect.”

Mass Action

In general chemistry, the law of mass action is meant to relate the masses, or mass changes, in a chemical reaction, to the chemical equilibrium. An early concrete example of the law of mass action was presented in 1864 by Waage and Gulburg.^[5] Therein they presented an equilibrium equation that resembles what is still used today. This concept inspired Arrhenius in describing ion dissociation.^[49] Both Arrhenius and Ostwald argued that an incomplete dissociation was the cause for deviations from a more direct concentration dependence on properties like molar conductivity, osmotic pressure, and freezing point depression.^[4,49] Hence, the “classical theory” describing interionic interactions, heavily relied on ion-pairing and the association constant, expressed as equation 1 for monovalent electrolytes:



where K_a is the association constant, c is the solute concentration, α is the fraction of free ions, c_M and c_X are the concentrations of cations (M^+) and anions (X^-) respectively, and c_{MX} is the concentration of the associated ions (MX). It is important to note that dissociation constants ($K_d = K_a^{-1}$) were preferred before mid-20th century. Hereafter, association (K_a) will be used to avoid confusion, and instead align with a more modern and logical terminology.^[50] Consequently, the concentration of associated ions, c_{MX} , follow the mass action law where the fraction of free ions, α , determines the relations between the concentrations of the different solutes, see equations 2 and 3:

$$c_{MX} = c(1 - \alpha) \quad (2)$$

$$c_M = c_X = c\alpha \quad (3)$$

These well-known expressions are often referred to in later literature as classical mass action. For conductivity, this relation attempts to capture the number of free ions in solution which can migrate in the presence of an electric field, whereas ion-pairs are not thought to contribute to this current. This is expressed in terms of molar conductivity, Λ , and limiting molar conductivity, Λ_0 , according to equation 4.^[51]

$$\alpha = \frac{\Lambda}{\Lambda_0} \quad (4)$$

Activity

In 1907, Lewis defined activity, a , as a translation factor between the free energy in a – real or fictional – ideal state and a non-ideal state.^[8] In modern terms: excess free energy or excess (electro)chemical potential. This concept has become fundamental for connecting thermodynamic principles to experimental results. The ideal state is here used as a reference state. An example of such reference state in electrochemistry is the standard reduction potential. Standard reduction potentials can either be obtained from a series of measurements, or calculated through a thermodynamic cycle.^[10] Activities allow for accurate predictions of measured potentials at any given concentration, based on the standard reduction potentials of the measured reactions. The activity of the electrolyte is related to its concentration in the general form:

$$a = (\nu_M^{\nu_M} \nu_X^{\nu_X}) c^{(\nu_M + \nu_X)} y_{\pm}^{(\nu_M + \nu_X)} \quad (5)$$

where one unit of dissolved salt produces ν_M and ν_X units of cations and anions respectively, and where y_{\pm} is the mean molar activity coefficient of the anions and cations.

The activity of an uncharged solute (non-electrolyte) is simply:

$$a = cy \quad (6)$$

where y is the activity coefficient of a non-electrolyte. The term ‘activity’ had been used before Lewis’ publication. However, it was previously employed to describe the mass action itself, considering associated ions as inactive, and free ions as active.^[49] Lewis diverged from this viewpoint, by suggesting that activities may have other peculiar concentration dependencies, drawing parallels to his earlier concept of fugacity for gases.^[52] Using a reference system in conjunction with a translation factor for relating to other systems should be seen as essential for anyone studying the energetics of a process or system. The strength (and weakness) of Lewis’ approach is that there is no need for an interpretation of what exact mechanism causes the changes in excess free energy. It is simply the matter of creating a framework that allows for a systematic comparison of processes that involves the energy of a system. In this regard the association constant, K_a , describes the equilibrium between

free and paired ions which is dictated by the energetics of the compounds, not simply the concentrations. Lewis highlighted this limitation of classical mass action and instead proposed a relation governed by activities, which for a monovalent electrolyte becomes.^[8]

$$K_a = \frac{a_{MX}}{a_M a_X} = \frac{y_{MX}(1-\alpha)}{c_{y_{\pm}}^2 \alpha^2} \quad (7)$$

A decade later, in a review titled “Activity Coefficients of Strong Electrolytes,” Lewis and Randall provided concrete examples where it became highly problematic to interpret the activity of an electrolyte as caused by ion association.^[9] In contrast, using activity coefficients in conjunction with a mass action expression allows for a constant association constant, K_a , since the activity coefficients of the free ions, y_{\pm} and paired ions, y_{MX} are expected to change with concentration. However, this also has the ramification that K_a , y_{\pm} , and y_{MX} can be treated as interdependent parameters. Considerations of aggregates of ions would of course introduce even more interdependent parameters, which would risk making a quantification ambiguous. A careful assessment, based on evaluations of different quantities, is therefore required to confidently relate electrochemical potentials, concentrations, and ion-pairing.

In their review, Lewis and Randall also present additional insights.^[9] For example, they highlighted the use of standard states related to infinitely dilute solutions. They also introduced the concept of ionic strength, I . That is, accounting for the charges of the ions, z_i , when considering their concentrations, c_i . Moreover, they asserted that in dilute solutions of “strong electrolytes” the activity at a given – dilute – concentration depends on the ionic strength rather than the chemical identity of the ions.

$$I = \frac{1}{2} \sum_i z_i^2 c_i \quad (8)$$

Despite extensive discussions by Lewis and Randall on activity coefficients, the underlying phenomenon influencing this excess free energy in strong electrolytes remained unclear. Two years later, Debye and Hückel resolved this gap with their theory on ionic attractions.^[1] While never crediting Lewis or Randall,^[53] the theory incorporated many concepts published in 1921. A key insight in 1923 was that ions are not randomly distributed in electrolyte solutions; positive ions are likelier to be surrounded by negative ions within a certain volume and vice versa, forming what is commonly known as the ionic atmosphere (or ionic cloud). They proposed an expression for the radius of this ionic atmosphere ($1/\kappa_d$).^[51]

$$\kappa_d = F \sqrt{\frac{2000I}{RT\epsilon_0\epsilon}} \quad (9)$$

where F is Faraday’s constant, ϵ_0 vacuum permittivity, ϵ dielectric constant, R is the gas constant, and T is the absolute temperature. While Lewis originally used molality as the concentration unit for the ionic strength, the use of molar

concentrations, c_i , was an important part of the derivation presented by Debye and Hückel. It is important to note that the ionic atmosphere will shrink as concentration increases, establishing a clear limit for the model’s validity. Specifically, when $1/\kappa_d$ becomes smaller than the ion size parameter, \bar{a} , (previously interpreted as the ions’ distance of closest approach, which has been deprecated),^[54] the theory breaks down. In fact, the model is expected to fail even before the ionic atmosphere is confined within the ions themselves.^[55]

For a detailed derivation of the final expression in terms of mean rational (mole fraction-based) activity coefficients, f_{\pm} , readers are directed to Robinson and Stokes’ book on electrolyte solutions.^[13] Nevertheless, Debye and Hückel’s general expression, is likely here presented clearest with variables of modern units, similar to what has been presented by Fawcett.^[51]

$$\ln f_{\pm} = \frac{-A|z_+z_-|\sqrt{I}}{1 + B\bar{a}\sqrt{I}} \quad (10)$$

$$A = \frac{N_L e_0^2}{\epsilon_0 \epsilon RT 8\pi} \frac{\kappa_d}{\sqrt{I}} = \frac{N_L e_0^2 F}{8\pi} \sqrt{\frac{2000}{(\epsilon_0 \epsilon RT)^3}} = 4.202 \times 10^6 \sqrt{\frac{1}{(\epsilon T)^3}} \quad (11)$$

$$B = \frac{\kappa_d}{\sqrt{I}} = F \sqrt{\frac{2000}{\epsilon_0 \epsilon RT}} = 5.029 \times 10^{11} \sqrt{\frac{1}{\epsilon T}} \quad (12)$$

where N_L is Avogadro’s number, e_0 is the charge of an electron, and \bar{a} is the ion size parameter. The coefficients obtained from Debye and Hückel’s expression can be converted to the molar or molal scale after the calculation. These additional expressions can also be found in Robinson and Stokes’ book on electrolyte solutions.^[13] However, the distinction between the concentration scales is usually not necessary. Neglecting the distinction tend to produce errors well below 1%. Ionic attraction theory is widely accepted as sufficient for predicting the mean activity coefficients of dilute electrolyte solutions. This indicates that it is indeed long-range electrostatic interactions between ions that dominate the activity of dilute electrolytes. This is in stark contrast with the 19th century view, where ion-pairing was believed to be the dominant factor governing the “active” and “inactive” ions.^[49]

Activity can be used to describe the free energy of any solute at any concentration. Both electrolytes and non-electrolytes (uncharged solute) can be assigned an activity coefficient linking the solutes excess free energy to the concentration. Figure 2 shows the rational activity coefficient for different solutes in water. Characteristic for electrolytes is the rapid decrease in activity coefficients as an infinitely dilute solution becomes more concentrated, which is captured by ionic attraction theory, a feature not shared by non-electrolytes. Non-electrolytes typically only give rise to short-range interactions in the solutions, this causes a linear concentration dependence in dilute solutions.^[13] How these short-range interactions will affect the free energy of the system will depend largely on the chemical nature of the solute and solvent. It is therefore likely hard to create accurate empirical predictions, of how the activity coefficients will change with concentration when the

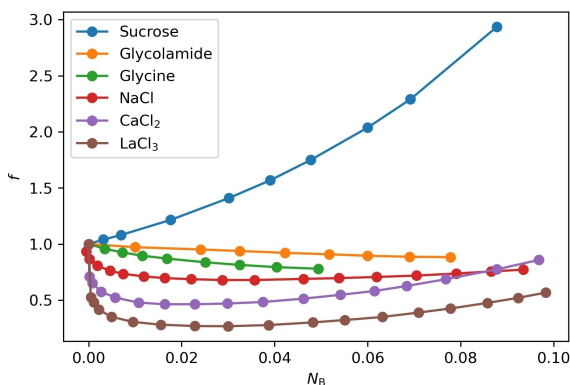


Figure 2. The rational activity coefficient, f , of the solute for some electrolytes and non-electrolytes plotted against the total mole-fraction concentration of the solute, N_B . The data was obtained from Robinson and Stokes' *Electrolyte solutions*.^[13]

system is dominated by dispersion, or dipole-dipole, or other short-range interactions. Moreover, as an electrolyte becomes more concentrated the short-range interactions become more dominant in these systems. These will eventually overshadow the long-range interactions described by ionic attraction theory.^[13] However, one might perhaps choose to link these short-range interactions to solvent shared and solvent separated ion-pairs, or perhaps even to contact ion-pairs.

Activity is actually often mentioned in contemporary battery literature, but it is seldomly utilized, nor is it discussed in detail. Yet, in many of these brief discussions there appears to be a confusion of critical consequence regarding the choice of standard state for electrolyte solutions. It is true that any state can be chosen for the standard state, however, the type of standard state needs to be kept in mind during a comparison of thermodynamic data. Moreover, some standard states are generally more useful than others. The most widely used standard state for electrolyte solutions is the *hypothetical unit concentration* standard state.^[10,13,16,56,57] This is a fabricated, or fictive, state where the electrolyte solution share many properties with the pure solvent, but the solute is imagined to have unit activity ($a = 1$, in the chosen concentration scale). To achieve this, the solutes activity coefficients are set to approach unity as the concentrations approach infinite dilution (Figure 2). In contrast, modern battery literatures appear to refer to a real concentration as the standard state. Unfortunately, the misconception between what has been commonly used as the standard state to report the potentials in older literature causes errors that often invalidates many thermodynamic reasonings in contemporary battery literature. For example, the potential of the reduction of silver chloride to pure silver and chloride anions in 1 mol/kg potassium chloride at 25 °C is 0.2352 V vs. standard hydrogen electrode, and not 0.2223 V, which is the value at the *hypothetical unit concentration*.^[10,13] Unknowingly comparing data obtained using different states will lead to artificial differences, that are simply caused by this difference in standard state. Moreover, there are certain expressions derived for the hypothetical unit concentration standard state, which would not be applicable for other reference states. For example,

the expression for converting activities obtained by freezing point depression to the activities at a different temperature using heat capacities and heat contents.^[13]

In summary, the use of activities together with a reference state allow for a systematic comparison of energy driven processes in solutions. This systematic approach appears to be less prominent in modern battery literature, despite its applicability for characterizing electrochemical reactions, and other thermodynamically driven processes in a battery cell. The use of activities can help to rationalize the energetics of the system, at any concentration. Yet, careful handling is required when relating the excess free energies to a concrete process, or to specific constituents within an ensemble. Still, a correct interpretation can lead to broader understanding of the processes within a system. This is exemplified by how the concepts from ionic attraction theory can be used to explain how the conductivity of a dilute electrolyte changes with concentration.

Conductivity

In 1923, Debye and Hückel also published an expression linking ionic attractions to the conductivity of dilute electrolyte solutions.^[58] Together with Onsager's corrections published in 1927,^[59] the final relation would later be called the Debye-Hückel-Onsager theory. As for the ionic attraction theory, the conductivity expression also makes use of the inverse radius of the ionic atmosphere κ_d . Here κ_d relates to how ionic attractions retards the movement of ions in an electrolyte solution. In fact, two concrete factors were hypothesized (a more in-depth, modern, description can be found by Boroujeni et al.):^[60]

(i) Relaxation Effect (B_1):

An electrostatic force acts between each ion and its respective ionic atmosphere. As the center ion moves its ionic atmosphere does not have time to relax, causing a distortion. This will impede the center ions movement, termed the relaxation effect B_1 .

$$B_1 = \frac{\Lambda_0 N_t |z_+ z_-| e_0^2}{12\pi\epsilon_0 \epsilon R T} \frac{q\kappa_d}{1 + \sqrt{q}} \quad (13)$$

(ii) Electrophoretic Effect (B_2):

The movement of the counter ion around a central ion will create an additional viscous force resulting in a retardation of the central ion's movement, known as the electrophoretic effect B_2 .

$$B_2 = \frac{N_t e_0^2 (z_+ + |z_-|) \kappa_d}{6\pi\eta} \quad (98)$$

Both effects are influenced by the ionic atmosphere. The electrophoretic term also includes the viscosity, η , of the pure solvent, while the relaxation is affected by the limiting molar conductivity, Λ_0 (conductance per mole of solute at infinite dilution). For a symmetrically valent electrolyte, the factor q is simplified to 0.5, the complete expression is:^[59,61]

$$q = \frac{z_+ |z_-| (\lambda_+ + \lambda_-)}{(z_+ + |z_-|) (\lambda_+ |z_-| + \lambda_- z_+)} \quad (15)$$

Here λ_+ and λ_- represent the individual molar ionic conductivities of the cation and anion, respectively. The final expression resembles that found by Kohlrausch in the 19th century:

$$\Lambda = \Lambda_0 - h\sqrt{c} \rightarrow \Lambda = \Lambda_0 - \left(\frac{B_1}{\sqrt{I}} + \frac{B_2}{\sqrt{I}} \right) \sqrt{I} \quad (16)$$

Thus, Kohlrausch constant h was given meaning in the Debye-Hückel-Onsager theory. The expression showed good agreement for dilute electrolytes, assuming full dissociation. However, it is crucial to note that both Debye and Hückel's expressions for activity coefficients and the conductivity expression are designed for fully dissociated dilute electrolytes. In a strong dielectric medium like water, this is often a reasonable approximation at low concentrations. However, it's essential to recognize that the ionic attraction theory doesn't disprove the existence of mass action. All electrolytes are expected to exhibit some degree of ionic association given a sufficiently high concentration. The challenge lies in determining when the ionic attractions become overshadowed by other effects, such as mass action. It is perhaps even questionable if such distinction is truly possible.

An early attempt to integrate ion-pairing with the theory of ionic attraction was made by Kraus and Fuoss in 1933.^[62] In their work, they introduced an activity based mass action term in the Debye-Hückel-Onsager theory:

$$\Lambda = \alpha(\Lambda_0 - \left(\frac{B_1}{\sqrt{aI}} + \frac{B_2}{\sqrt{aI}} \right) \sqrt{aI}) \quad (17)$$

$$K_a = \frac{(1 - \alpha)}{c y_{\pm}^2 \alpha^2} \quad (18)$$

$$\ln y_{\pm} = \frac{-A |z_+ z_-| \sqrt{aI}}{1 + B \sqrt{aI}} \quad (19)$$

In their approach, the limiting molar conductivity, Λ_0 , association constant, K_a , and an ion-pair corrected mean molar activity coefficient, y'_{\pm} , were solved by an iterative process. Kraus and Fuoss argued that in the dilute solutions that were considered, the activity coefficients of the ion-pairs would be close to unity. Thus, they chose to simplify the expression by omitting this additional parameter. While promising, the method to solve for ion-pairing and limiting molar conductivity was later approximated by an interpolation table by Fuoss in 1935 to streamline the tedious iterative computation.^[63] This method, in fact, is what Kraus appears to have used to gather data on limiting molar conductivities and dissociation constants, in a variety of electrolyte solutions of different solvents. Data, which has historically been considered reputable references.^[13,64-66]

The ion-pair corrected mean molar activity coefficient can also be derived from the total free energy and the mean molar activity coefficient y_{\pm} as shown by Robinson and Stokes.^[13] For simple monovalent electrolytes the expression simplifies to:

$$y_{\pm} = \alpha y'_{\pm} \quad (20)$$

The derivation of the equation above can be found in Robinson and Stokes' book, along with a general expression.^[13] It is noteworthy that this relation is not consistent with Kraus and Fuoss' introduction of dissociation in the Debye-Hückel equation. A numerical difference arises when comparing the two approaches, though it may not be a critical issue. However, the expression based on the total free energy is likely a more just treatment when adjusting the activity coefficient for ion-pairing. The total free energy of the system should not depend on the perception of the system; hence this treatment is simply a mathematical construct that allows for a partitioning of the solutes free energy based on the perceived number of different solutes. In principle, an expression could be derived to also include ion-agglomerates, but it is questionable if a scenario arises to justify this procedure since it will make the analysis more ambiguous.

In the latter half of the 20th century, Fuoss, among others, developed more advanced expressions to describe the concentration dependence of conductivity.^[67,68] These essentially expand on Onsager's formulation and are generally presented as:

$$\Lambda = \Lambda_0 - S\sqrt{c} + E \log c + Jc \quad (21)$$

Which can be modified to account for mass action by:

$$\Lambda = \Lambda_0 - S\sqrt{c\alpha} + E \log c\alpha + Jc\alpha + K_a c \alpha^2 y_{\pm}^2 \Lambda \quad (22)$$

Justice has provided a summary of various formulations for the parameters S , E , and J .^[61] Despite improvements, these expressions are not expected to be accurately representative at 1 mol/L, a concentration commonly used in experiments for battery electrolytes. The added complexity also makes the understanding of interionic interactions less intuitive and accessible to a broader audience. The introduction of ion association in equation 20 is also a bit problematic, because the J parameter and association constant can be viewed as interdependent.^[37,54,61] Such ambiguity naturally leaves room for a broader interpretation of ion-pairing, by for example implicitly incorporating non-contact pairs in a mass action term.

The 20th century saw many advancements in our understanding of how an electrolyte's conductivity changes with concentration. Arguably, the early Debye-Hückel-Onsager theory may still be the most useful expression considering its simplicity while still being qualitatively representative. Especially since the more advanced expressions still are not expected to be accurate for concentrations commonly employed in electrolyte solutions for batteries. The more advanced formulations (equation 21 and 22) may enable a discussion on how different non-contact ion pairs affect the conductivity, which may serve as a link to the modern discussions about ion-

paring and conductivity. Yet, it is interesting that on this specific topic, in the 20th century, there is seldom any mentions of the Walden's rule (except for infinitely dilute solutions) or how viscosity of the electrolyte solution is affecting the conductivity at a real concentration. That is, these concepts that are often considered in modern literatures do not appear to explicitly build on the ion-transport framework that was developed during the 20th century by Falkenhagen, Onsager, Debye, Hückel, Fuoss, Lewis, Justice and many more.^[37,55,58,61,69,70]

Comparing Ion-Pairing and Activity Coefficients

Certain phenomena could likely be explained equally well using either ion-pairing or activity. The best explanations could perhaps even be achieved by combining ion-pairing and activity argumentations. Issues may, however, appear if mass action is incorrectly assumed to be a dominant factor in the electrolyte solution, even if activity coefficients are included. Take the example of sodium acetate in water: examining the conductivity in Figure 3a reveals a clear maximum around 3 mol/L. Such behavior is often attributed to ion-pairing in modern literature. Despite attempts, it seems challenging to use the Fuoss-Kraus method to obtain the dissociation constant and limiting molar conductivity. Arguably, this difficulty could stem from an overly dominant ion-pairing. Relying entirely instead on mass action, by using an activity corrected Ostwald conductivity expression (combining equation 4 and 7), this superficial fit yield $K_a = 3.5$ and $\Lambda_0 = 91$, resulting in the fit in Figure 3b.

Based on the fit to the data, only assessing the concentration dependency of the conductivity solely by mass action – at first glance – appears to be reasonably representative. The activity corrected Ostwald expression might even be considered to fit qualitatively at moderate concentrations. The divergence at higher concentrations could simply be due to the formation of ion aggregates. In essence, the presented approach and reasoning in handling ion-pairing is somewhat representative for contemporary literature. However, the correction for activity

coefficients are usually omitted. Nevertheless, as shall be demonstrated, this conclusion is questionable!

Considering the relationship between ion-pairing and the perceived activity coefficient (Equation 20), it would be expected that activity coefficient of free ions, γ'_{\pm} , follows Debye-Hückel behavior at low concentrations. Conversely, by not compensating for the mass action, the observed activity coefficient, γ_{\pm} should display an exaggerated initial slope at low concentrations (Figure 4a).

Compensating the activity coefficients of sodium acetate in water for mass action, with $K_a = 3.5$, causes a noteworthy behavior. When accounting for mass action, the free sodium acetate ions γ'_{\pm} exhibit behavior more akin to a non-electrolyte than actual free ions (Figure 4b, and Figure 2). That is, concluding that moderate ion-pairing occurs in this system would mean that the dissociated solute behaves more like a molecule than an electrolyte. This cannot be the case! Association is here used as an inappropriate substitute for electrostatic interactions. Unfortunately, the measured data does not appropriately cover the range for ionic attraction theory. Yet, assuming that ionic attraction theory is valid below a certain concentration (for example where $1/\kappa_d \leq 1.9 \times 10^{-10}$ m) a smooth monotonic transition would be expected between the theoretically derived and measured coefficients. Figure 4a show a deviation between γ_{\pm} obtained from ionic attraction theory and the literature data already at the first measurement point around 0.1 mol/L. Yet, by visual interpolation it seems at least possible to obtain a smooth monotonic transition between the measured and theoretical values if mass action is not included. In contrast, the deviation is even more significant when compared to the activity coefficient one would expect to observe at a mass action of $K_a = 3.5$, denoted as $\alpha\gamma'_{\pm}$. Moreover, the transition would not be monotonic since the interpolation would need to pass through a minimum to allow for a smooth transition between the theoretical and measured values. Hence, an ion-association constant of $K_a = 3.5$ results in questionable outcomes both in the dilute limit and at higher concentrations. This does not

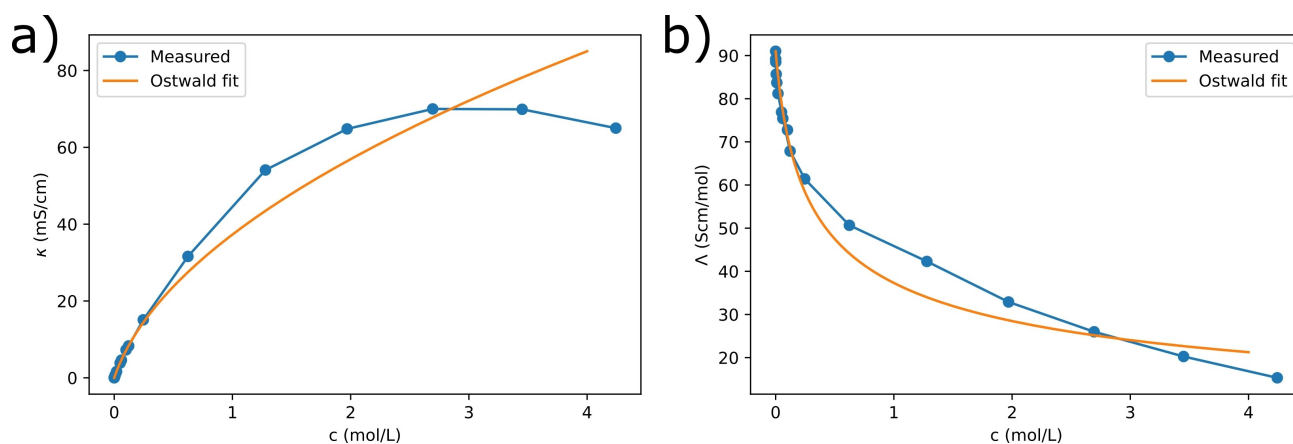


Figure 3. Conductivity of sodium acetate in water, and Ostwald conductivity at $K_a = 3.5$ and $\Lambda_0 = 91$, obtained by combining equation 4 and 7 with $\gamma_{MX} = 1$. The data was obtained from the CRC-database.^[71] a) The conductivity, κ , against molar concentrations; b) The molar conductivity against concentration. A closer look at low concentrations would reveal that the fitting is rather poor. In reality, there is no truly good fit for these measurements using solely mass action.

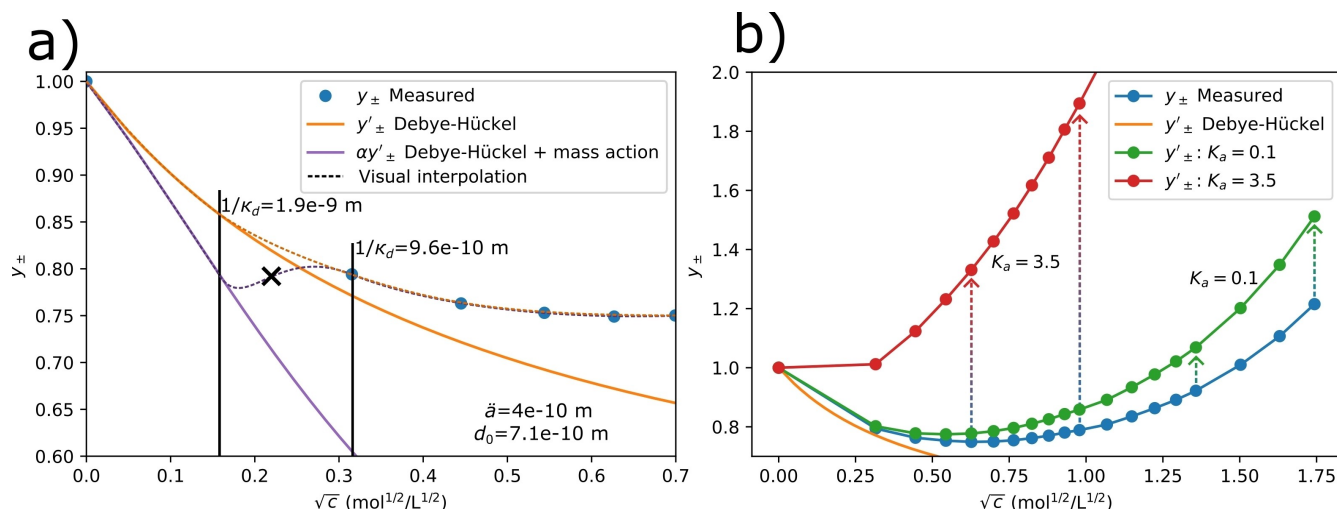


Figure 4. A comparison of measured mean molar activity coefficients of sodium acetate in water, with coefficients obtained from Debye and Hückel's equation with and without the considerations of ion-pairing. a) The measured activity coefficients of sodium acetate in water compared with the expected coefficients from ionic attraction theory with and without a compensation for an association constant of $K_a = 3.5$. The dashed lines represent visual interpellations between the theoretical expressions and the measured data starting from a point where ionic attraction theory is assumed to be valid. This assumption is based on the size of the ionic atmosphere, $1/\kappa_d$, ion size, \bar{a} , and the distance of mutual potential between two ions, d_0 .^[55] b) The measured activity coefficients of sodium acetate in water compensated for an association constant of $K_a = 3.5$ and $K_a = 0.1$. The graph also contains prediction of ionic attraction theory for a fully dissociated electrolyte. The data was obtained from Robinson and Stokes electrolyte solutions and converted to molar activity coefficients by using density data from the CRC-database.^[13,71] There is a mismatch of 5 °C between the two datasets. There was not enough data available to properly correct for this. Still, this difference is not expected to affect the overall conclusions.

imply that ion-association does not occur at all in this electrolyte solution, but it is more likely to be in the range of $K_a \leq 0.1$ (Figure 4b). In this scenario, it is probably more appropriate to initially consider electrostatic interactions in conjunction with other short-range interactions.

Effects in Concentrated Solutions

The state-of-the-art theory for electrolytic conductivity from 1960–1970, while reaching high complexity, still lacks the ability to account for commonly used concentrations. This might be a reason for the apparent return of contemporary research to the 19th century treatment. As demonstrated, the mass action-centered approach seems reasonable, if not sufficiently scrutinized. Classical mass action is, however, intuitive and easy to understand. It aligns well with a particle and mechanism-centered view of chemistry prevalent in modern literature. This alone might justify the use of a bygone treatment of electrolyte solutions.

If a system has a strong tendency to form ion-pairs, mass action would indeed dominate conductivity at high concentrations. However, even when mass action is disregarded, there are still effects to consider. Firstly, secondary effects from the electrophoretic effect and ion relaxation become more prominent at higher concentrations, which is partly captured by equation 21. Moreover, at higher concentrations, long-range interactions are overshadowed by short-range interactions, which can be seen from how the excess chemical potential evolves with concentration (Figure 2). This would also likely affect the conductivity in a peculiar manner. Finally, how the

dielectric medium changes with electrolyte concentration also needs to be considered.

As an electrolyte solution becomes more concentrated, the dielectric constant of the solution tends to decrease.^[13] This macroscopic decrease in dielectric constant is thought to be caused by the solvent molecules close to the coordinated ion, which is called a region that undergoes dielectric saturation. For monovalent electrolytes in water, the dielectric saturation is believed to occur in the first solvation sphere around the ion. Beyond this point the medium would maintain a value of the dielectric constant close to that of the host solvent.^[72] This is, in fact, a premise for the ionic attraction theory where the host solvent's dielectric constant is used to account for the dielectric shielding between the ions. Already in their original publication, Debye and Hückel stated that this treatment would lead to errors for concentrated solutions.^[1] Inevitably, at a certain concentration, there would not be enough solvent in the system to maintain the host solvents value of the dielectric constant between the ions. This would lead to a drastic change in ion-shielding, which would likely have a profound impact on ion-transport in the system. Yet, simply concluding that such concentrated systems contain several solvent-separated ion pairs (which would be the case), would arguably fail to portray this effect.

In particular for concentrated solutions, there is promise in using ion-transport matrices to trace the changes in ion-transport with concentration. Miller showed the potential of this approach already in 1966.^[73] These matrices, similar to those later employed by Newman, rely on expressions that incorporate activity coefficients.^[16] Thus, characterizing activities is important for the future success of this approach.

The excessive reliance on ion-pairing may result in strictly erroneous conclusion about the nature of electrolyte solution. Most electrolytes, that can be sufficiently concentrated, produce a maximum in the conductivity (Figure 3a). This maximum is often erroneously claimed to be caused by ion-pairing. A classical mass action expression will never produce a maximum in conductivity as a function of concentration. Theoretically, the conductivity would always increase with concentration in a model solely based on classical mass action, which can easily be shown using Equation 1 and 4 (see Supporting Information).

Another inappropriate practice is to use the ratio between measured conductivity and one obtained from the Nernst-Einstein relation with self-diffusion coefficient data and relate this to the degree of ion association. The Nernst-Einstein relation is only valid at infinite dilution. At a real concentration, self-diffusion and conductivity are distinct transport properties. It is not possible to predict a conductivity from self-diffusion data by simply accounting for ion-pairing.

The main point of using standard states with excess free energies and in extension activity coefficients, is to enable a comparison of processes in different systems. For electrolyte solutions the easiest and most useful point of comparison is often towards the infinitely dilute solution. This is largely why properties in infinitely dilute solutions have been studied extensively for aqueous solutions historically. This is also why *hypothetical unit concentration standard states* have been employed extensively in the 20th century.^[10,13,16,56,57] A trend observed in many studies within the contemporary battery community is a tendency to focus on relatively concentrated solutions. This often limits the scope of understanding. The absence of reference experiments in dilute solutions, with appropriate extrapolations, often make the conclusions less reliable and difficult to compare with other studies and systems. The concentrated solution may be of greatest interest, but to properly study concentrated solutions it is often necessary to compare the results with dilute solutions.

The lack of reliable and standardized studies on electrolyte solution for batteries appear to have caused a misaligned intuition within the community. For example: thermodynamic factors, which can be derived from activity coefficients, are occasionally theoretically evaluated in unreasonable ranges.

Electrolyte solutions are often studied at concentrations where any form of ion-pairing is inevitable due to simple arithmetic, which is often overlooked in favor of more exotic speculations.

There also seems to be a misalignment in intuition about how different ion-transport properties are expected to change with concentration. For example, transference is usually expected to display a modest concentration dependence compared to conductivity and diffusion.^[14,74,75] It is concerning when modern studies present a more drastic concentration dependence without clear reflection on this deviation, often solely attributing it to ion-pairing without substantial evidence.

The presented issues can be remedied by a combined effort in the battery community to standardize experiments in the same manner that has been done for aqueous system in the 20th century. Activity coefficients could here again be used as a

key parameter. It will require a significant effort to catch up with the vast amount of data collected for aqueous systems. Especially as there exists only one aqueous solvent, compared to the vast number of interesting organic solvents. Still, modern technology should make it easier to conduct more accurate experiments quickly and create more advanced models, compared to what was possible a century ago!

Conclusions

The ambiguous nature of the treatments of ion-pairing has been debated throughout the 20th century. As here shown for sodium acetate in water, a seemingly adequate match to conductivity data can evidently be obtained regardless of the soundness of the chosen model. Yet, this does not suffice for developing a better understanding for the intricacies of ion-transport and electrochemical potentials in electrolyte solutions. A satisfactory interpretation should yield consistent results when applied to different phenomena, be it ion-transport or free energy changes of the system.

In this regard, the ionic attraction theory and Debye-Hückel-Onsager theory may serve as a prime example for a framework describing dilute electrolyte solution with low ion association. Developing a more general theory may likely be a great challenge, or even impossible in the established framework. Still, overemphasizing ion-pairing, while disregarding other interionic or intermolecular interactions, likely does a disservice to the scientific community.

A more nuanced approach, comparing different interconnected phenomena, with a clear connection to the established theory will likely enable deeper understanding of electrolyte solutions. Perhaps it will even be necessary to partially discard the 20th centuries theories, in favor of new models. Yet, a profoundly new model will gain credibility if the inventors display a clear understanding of the historical theories.

Access to consistently defined activities and standard states in organic electrolyte solutions will likely help the development of new theories. If nothing else, this information would allow for better comparisons of experimental results and allow for predictions based on thermodynamic data.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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