

# Ion Trios: Cause of Ion Specific Interactions in Aqueous Solutions and Path to a Better pH Definition

Peter M. May\* and Eric F. May

Cite This: *ACS Omega* 2024, 9, 46373–46386

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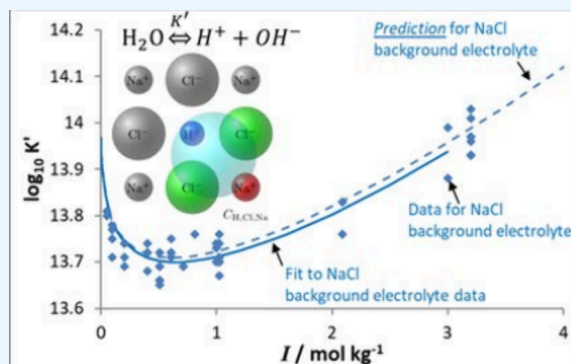


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**ABSTRACT:** Many important thermodynamic calculations for aqueous systems are profoundly limited because ion specific interactions have not been understood. Here an alternative modeling paradigm with compelling advantages is presented based on fundamental insights regarding ion–ion interactions at higher electrolyte concentrations. We also show how an intense ongoing controversy regarding single ion activity coefficients (SIACs) can be resolved and how SIACs can be quantified in full thermodynamic compliance using an overlooked convention. SIAC values can in fact be determined unequivocally and compatibly from two independent types of measurement at trace concentrations. These developments promise important advances, especially in defining pH and modeling multicomponent aqueous systems.



## INTRODUCTION

In 1923, Debye and Hückel<sup>1,2</sup> (DH) showed that in dilute aqueous solutions the activity coefficients of ions are determined by the electrostatic attraction between ions of opposite charge. Since then, scientists have struggled to advance the fundamental understanding of strong aqueous electrolyte solutions, failing to produce a broadly accepted theoretical consensus.<sup>3</sup> A stalemate has developed due to an entrenched focus on just two interacting ions. In contrast, we propose that with increasing concentration each cation–anion couple is soon impacted by other ions in their vicinity. Pair-wise attractions thus decrease, and are ultimately often overwhelmed, by the influence of a third ion drawn toward one participant in each primary association but significantly repelled by the other. Although higher order ionic interactions are widely presumed, their quantification has proved theoretically intractable and hence impractical for systems with higher electrolyte concentrations. Our “ion trio” phenomenon has not hitherto been recognized because its effects cannot be distinguished in solutions with just two kinds of ion. It manifests clearly only in electrolyte mixtures and they have not been given sufficient attention. However, the general patterns of physicochemical behavior in common ion mixtures as summarized herein provide conclusive evidence for these three-body interactions.

This insight has practical value because it improves predictions in electrolyte mixtures, particularly of mean ionic activity ( $\gamma_{\pm}$ ) and osmotic ( $\phi$ ) coefficients but also of apparent molar volumes ( $V^{\circ}$ ) and heat capacities ( $C_p^{\circ}$ ). Solubility, density, pH, and other thermodynamic calculations have been frustratingly inadequate for seawater, hydrometallurgical

liquors, surfactant, and colloidal solutions of polyelectrolytes, as well as body fluids like urine. In such cases, described briefly in the [Supporting Information](#) (SI), thermodynamic properties can only be accurately modeled by numerical fitting,<sup>3</sup> a serious problem given the inescapable sparsity of experimental data for multi-ion mixtures.

There are two main reasons for this failure to progress the thermodynamic description of aqueous electrolyte solutions in systems of practical interest and concentration. Both concern issues that have persisted despite their technological importance<sup>4</sup> and much contentious debate.<sup>5,6</sup> First, sound predictions require a better understanding of the fundamental effects which differentiate the characteristics in solution of salts having the same charge type, known as “ion specific interactions” (ISI) or “specific ion interactions”. This represents a “bemusing” failure<sup>7</sup> of physical chemistry, as true today as it was when Aaron Klug, Nobel Laureate 1982 noted in reference to ISI: it is “well-known to biologists that the [DH] theory, and by implication its extensions, [are] limited to slightly contaminated water”.<sup>7</sup> Second, single ion activity coefficients (SIACs) are often used to quantify how the  $\gamma_{\pm}$  for dissolved electroneutral substances is split between ions into  $\gamma_{+}$  and  $\gamma_{-}$ , where  $\gamma_{\pm} = (\gamma_{+} \gamma_{-})^{1/2}$  for 1:1 electrolytes, but

Received: August 14, 2024

Revised: October 16, 2024

Accepted: October 21, 2024

Published: November 5, 2024



there is no agreement about how best to define such single ion properties, or even whether this is sensible.<sup>8–10</sup> Sometimes described in the literature as “individual ion activity coefficients”, SIACs have been the subject of a remarkably intense controversy as described below and in the SI.

While most chemists believe intuitively that SIACs are physically meaningful, the International Union of Pure and Applied Chemistry (IUPAC) currently asserts that they are immeasurable.<sup>11</sup> As a result, no universal definition of pH is accepted<sup>12–15</sup> and the protocols used to define pH by national and international standards organizations have had to be repeatedly revised;<sup>16–20</sup> yet, they remain unsatisfactory as detailed below.

Answers to these worrying dilemmas can be found in an elaboration of the ion trios concept. We demonstrate here that aqueous physicochemical properties become dominated not just by “ion1–ion2” pairing, or by “short-range” forces, (as is so often assumed) but by “ion1–ion2–ion1” and “ion1–ion2–ion3” interactions in pure and mixed electrolyte solutions, respectively. Ion trios do **not** represent the formation of a new (triplet) species; they comprise two ions of like charge interacting, on average and at distance, with the same counterion as well as with each other. Nearest neighbor ions ameliorate the electrostatic attraction between cation and anion pairs and do so in ways that allow individual ion attributes to be distinguished. Thus, ISI can be explained and SIACs are shown to be physically sound quantities. A superior metrological quantification for pH can also be promulgated as a result.

## ION SPECIFIC INTERACTIONS

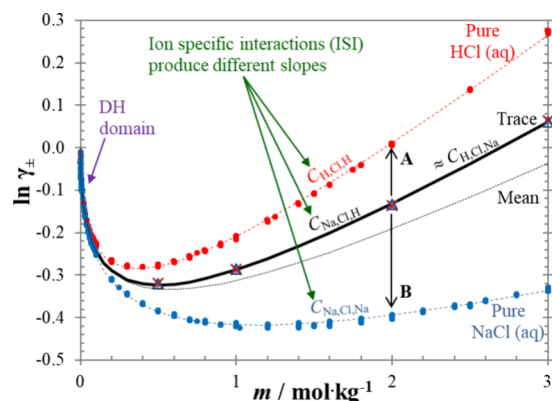
Data for around 200 single strong electrolyte solutions (SSES), *i.e.*, the pure binary systems comprising one salt plus water, have been described in the literature,<sup>21–23</sup> yielding the characteristically shaped curves for  $\gamma_{\pm}$  as a function of concentration seen in Figure 1 and in the SI.

Ion specific interactions become important beyond the DH domain<sup>24,25</sup> ( $I \leq 0.1 \text{ mol kg}^{-1}$ ) but there is as yet no convincing explanation for the differences exhibited between electrolytes.<sup>4,7,22</sup> After taking account of effects due to concentration,  $\gamma_{\pm}$  quantifies the interactions between ions. When  $\gamma_{\pm} < 1$ , the net interactions are attractive and the solution is more stable (lower Gibbs energy) than an ideal system of the same composition, whereas  $\gamma_{\pm} > 1$  implies that energetically unfavorable interactions dominate overall. Effects associated with solvation have been suggested<sup>22</sup> as a possible cause of the different slopes observed, but coulombic repulsions are a more plausible alternative, which has been glaringly neglected despite longstanding experimental evidence.<sup>26–28</sup>

Central to our present thesis are the mean ionic activity coefficients measured at trace concentrations,  $\gamma_{\pm}^{\text{Tr}}$ . Traditionally,  $\gamma_{\pm}^{\text{Tr}}$  are determined experimentally by extrapolation using the well-established, empirically-linear rule of Harned,<sup>21,22,29</sup> which holds that for two strong electrolytes, *MK* and *NK*, in a common ion (*K*) mixture

$$\begin{aligned} \log \gamma_{\pm}(\text{MK in NK}) \\ = \log \gamma_{\pm}(\text{MK}) - \alpha_{\text{MK}}(m) \times [1 - x] \times m \end{aligned} \quad (1)$$

Here,  $\alpha_{\text{MK}}(m)$  is a measurable, concentration-dependent, proportionality constant;  $m = m_{\text{MK}} + m_{\text{NK}}$  is the mixture's



**Figure 1.** Mean ionic activity coefficients in aqueous solutions of hydrochloric acid (HCl), sodium chloride (NaCl) and their mixtures. The mixture data points are taken from Robinson and Stokes.<sup>22</sup> Red dashed curve is  $\ln \gamma_{\pm}$  of pure HCl(aq), blue dashed curve is  $\ln \gamma_{\pm}$  of pure NaCl(aq), and dotted black curve is their arithmetic mean; red crosses are  $\ln \gamma_{\text{HCl}}^{\text{trace}}$  in NaCl; blue triangles are  $\ln \gamma_{\text{NaCl}}^{\text{trace}}$  in HCl; and the solid black line is the Trio model description of the *two* trace conditions. The path labeled by A represents the transition of NaCl and HCl mixtures at fixed total concentration,  $m$ , from trace HCl in NaCl to pure HCl, *i.e.* as the mole fraction of HCl increases from 0 to 1; path B represents the transition of NaCl and HCl mixtures from trace NaCl in HCl to pure NaCl, *i.e.* as the mole fraction of NaCl increases likewise.

fixed total molality; and  $x = m_{\text{MK}}/m$ . Thus, Harned's rule operates over so-called concentration “transects” such as those in Figure 1 marked A and B.

The experimental pattern expressed by eq 1 and illustrated in Figure 1 has been systematically and thoroughly investigated.<sup>30</sup> Overlap of the *two* trace activity coefficient curves is striking and exhibited by many 1:1 strong electrolyte mixtures. Distinctive common behaviors are similarly conspicuous in multivalent systems as described below. Robinson and Stokes,<sup>22</sup> and others (see, *e.g.*, ref.<sup>21</sup> pp. 604–607), appreciated the palpable theoretical connotation of these general observations but no satisfactory explanation has hitherto been forthcoming.

To model  $\gamma_{\pm}$  numerous theoretical models have appeared in the literature.<sup>3</sup> Every current framework for electrolyte thermodynamics is predicated on Brønsted's empirical principle,<sup>31–34</sup> which holds that in dilute solutions the effects of other ions with like charge can be neglected, so thermodynamic models generally assume that cation–anion attractions are primarily responsible for  $\gamma_{\pm}$ . As Brønsted recognized,<sup>31–34</sup> however, the principle is evidently inapplicable at higher concentrations,<sup>34</sup> especially when  $\gamma_{\pm} > 1$ . Cation–anion interactions are nevertheless the essential focus of Pitzer<sup>35–37</sup> and specific ion-interaction theory (SIT),<sup>38–41</sup> the two modeling frameworks most widely used and authoritatively recommended<sup>20,39–41</sup>

The Pitzer equations<sup>35–37</sup> seek to parametrize SIAC effects in a pairwise and multibody approach analogous to the virial equation for gases (SI). In mixtures, this soon leads to a combinatorial explosion of coefficients; consequently, Pitzer equations have too much flexibility and extrapolate badly. Pitzer frameworks also suffer from other flaws<sup>42</sup> (*e.g.*, multiple incompatible variants and irregular ternary parameters). Without a sound fundamental understanding of ISI, modeling calculations to date can only describe chemical systems of interest empirically. While the Pitzer equations can typically

reproduce the sets of experimental data used to train them (*i.e.*, by numerical determination of parameters) their results under other conditions frequently go astray. As is well-known, flexible empirical functions tend to forecast badly. This is a fatal weakness when dealing with any multicomponent system that spans ranges of component concentrations, temperature, and pressure. Modeling functions must be mathematically highly constrained to prevent unphysical predictions.

The SIT equation<sup>38–41</sup> on the other hand has only one adjustable parameter at 25 °C. Based on a theoretical model for ion specific interactions<sup>31,32,38,43–46</sup> and on the Bates–Guggenheim convention<sup>17</sup> (B-GC) for SIACs, SIT has been adopted by IUPAC for defining pH<sup>20</sup> and for estimating conditional equilibrium constants,  $K'$ , of reacting chemical species at trace concentrations in SSES solutions.<sup>40</sup> Unfortunately, SIT is grossly inaccurate for many of the SSES themselves<sup>47</sup> and, thus, cannot be coupled properly with activity quotients in equilibrium calculations when reactant concentrations rise above trace levels. The use of a single adjustable parameter means SIT has insufficient flexibility for general modeling purposes. Moreover, the ISI hypothesis<sup>22,39</sup> on which SIT is founded predicts (from pairwise interactions only) that the trace activity coefficients should follow the mean path between the parent SSES; as can be seen in Figure 1, they do not.<sup>22</sup>

**Single Ion Activity Coefficients.** Literature coverage has for decades been sharply divided between two beliefs: on the one hand that SIACs are physical quantities similar to other thermodynamic properties defined methodologically (*e.g.*, by extrapolation to infinite dilution) and, on the other, that they are a mere algebraic convenience, necessarily dependent on an arbitrarily chosen extra-thermodynamic assumption which cannot be validated, or even distinguished, by physical measurements. Modern chemical opinion has rarely been so divided and so confused for so long. The irreconcilable and acrimonious dispute has seen at least two journal editors attempt to put a stop to it.<sup>5,6</sup> At one point it was even agreed not to call any given quantity a single ion activity<sup>48</sup> yet the concept continued to be freely used, particularly in electrochemistry.<sup>49</sup> The schism<sup>5,6</sup> has become a philosophical and semantic ordeal for the solution chemistry community. One may well wonder, for example, how can theoretical inconsistencies arise in SIAC (or pH) values when the SIAC convention is axiomatic?

Many aqueous chemical properties are found to depend on the individual chemical species in solution, pH being a particular case. Solution color is often determined by single ions with unique chromophores, while electrochemistry hinges on electrodes sensing certain ions. Acidity depends on the relative abundance and energy of interaction of hydrogen ions, as quantified by the concentration  $m(\text{H}^+)$  and activity coefficient  $\gamma_+(\text{H}^+)$ , respectively. Much knowledge has accumulated<sup>50</sup> on the distinct role of  $\text{H}^+$  and other chemical species in the equilibrium quotients of reactions, such as the familiar weak acid dissociation constant quantified by its concentration and activity coefficient (*e.g.*,  $K_{\text{HA}} = \{\text{H}^+\} \times \{\text{A}^-\} / \{\text{HA}\}$  for  $\text{HA} \leftrightarrow \text{H}^+ + \text{A}^-$ , where  $\{\}$  denotes the activity of each species, as in  $\{\text{H}^+\} = m(\text{H}^+) \gamma_+(\text{H}^+)$ ). The chemistry of electrolyte solutions is thus intuitively seen to reflect the intrinsic nature of the constituent ions as separate entities. Furthermore, for reasons of practicality, especially in chemically reactive systems, modeling frameworks for multicomponent electrolyte

solutions are driven to quantify the chemical potentials of constituent ions using SIACs.

However, *chemical activities and equilibrium constants are thermodynamic quantities*. Due to electroneutrality, SIACs are not thermodynamically independent: a mathematical link between them must be introduced as part of their definition. Consequently, SIACs cannot be *measured* without invoking some convention or extra-thermodynamic assumption to disconnect the electroneutral components used in the Gibbs phase rule (SI). Many of the arguments for SIACs in the literature have ignored this. On the other hand, in thermodynamics, *there is nothing unusual about conventions that establish a scale for absolute numerical values of particular properties*. Any convention where the single ion contributions to a thermodynamic property combine to give the observed values for the electrolyte is mathematically permissible<sup>51</sup> but this is not sufficient: a sensible convention for a SIAC should preserve *as far as possible* the individual nature of ions discussed above and do so unambiguously. MacInnes' well-known convention,<sup>52</sup> where  $\gamma_+(\text{K}^+) = \gamma_-(\text{Cl}^-) = \gamma_{\pm}(\text{KCl})$  in pure  $\text{KCl}(\text{aq})$  at all concentrations, illustrates a common pitfall because it leads by different paths to chemical oddities and numerical conflicts (SI) in electrolyte solutions without  $\text{K}^+$  and  $\text{Cl}^-$ .<sup>53</sup> It is the implementation of the convention, not the convention itself, that miscarries. This distinction (SI) is essential to resolving the dispute over SIACs.

So, the apparently contradictory SIAC beliefs described above are both arguable as stated but they can in fact be married harmoniously, and usefully, by any realistic molecular-level description of SIACs based on the adoption of a sensible convention. Avoiding, in particular, conventions that imply that the chloride ion's properties at a given ionic strength are independent of the solution composition should be used as a guiding principle in the selection of a practical convention.

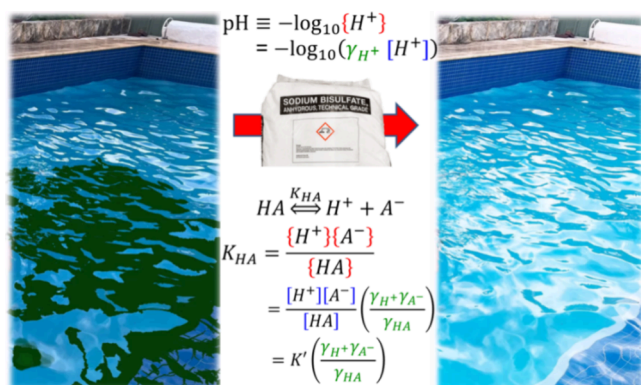
**pH Uncertainties and Thermodynamic Modeling Implications.** Through the solubility and bioavailability of many nutrients and toxins, almost every natural process occurring in water solutions depends on pH, which is consequently the most frequently measured of all physicochemical properties.<sup>9,12</sup> However, the current IUPAC pH definition<sup>20</sup> is based on the B-GC<sup>17,20</sup> which specifies ("notionally"<sup>11</sup>) that the chloride ion SIAC is the same in every SSES at constant ionic strength,  $I = 0.5 \sum_i m_i z_i^2$ , where  $m_i$  and  $z_i$  are the molality and charge of each ion present in the solution. That assumption is unrealistic<sup>13,20</sup> and, when implemented, it results in thermodynamic inconsistencies<sup>53</sup> that seriously limit the scope<sup>20</sup> of applications to dilute solutions ( $I \leq 0.1 \text{ mol kg}^{-1}$ ) with  $2 < \text{pH} < 12$ . Scientifically, a robust definition is needed especially for reliable determinations of ocean acidification and carbon dioxide ( $\text{CO}_2$ ) uptake because current uncertainties inherent in the definition<sup>12,14,20,54</sup> prevent oceanographers who model these processes from achieving the required accuracy.<sup>12,14,54–57</sup>

Of course, the uncertainties impacting pH apply to every ion in solution, not just  $\text{H}^+$ . This is why thermodynamic modeling in general has been beset by inaccuracy. To predict changes in pH, solubility, and other physicochemical properties, it is necessary to have a theoretical framework, which represents the changes in activity of all chemical species in solution. Such a model must align with the numerous chemical equilibria, which generally control the relative concentrations of these species. The vast majority of thermodynamic frameworks for



aqueous systems minimize Gibbs energy by solving a set of “mass balance equations” coupled with recognized equilibrium constants for every unique chemical reaction occurring in the solution. For systems at finite concentration, the available equilibrium constants have usually been determined for reactants and products at trace concentrations within a background of a supposedly nonreactive strong electrolyte like NaCl, present at much higher concentrations. As just indicated, however, even though the “spectator ions” are not involved directly in the reaction, the values of the measured equilibrium constants depend directly on the “background” electrolyte concentration via activity coefficients. There is consequently a complicated interplay of mathematical relationships and uncertainty propagations related to the different ISI in both measured and modeled systems.

Consider for instance a thermodynamic calculation to predict the pH of swimming pool water. Many chemical equilibria operate even in this relatively simple example, including those of  $\text{CO}_3^{2-}$  (from atmospheric  $\text{CO}_2$ ) reacting directly with cations such as  $\text{H}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ . Since it is impractical to quantify the required equilibria experimentally under all possible circumstances, the relevant so-called<sup>38</sup> “conditional” equilibrium constants,  $K'$ , must be predicted using a modeling framework. Each and every  $K'$  depends on a quotient (product) of SIAC values as depicted in Figure 2.

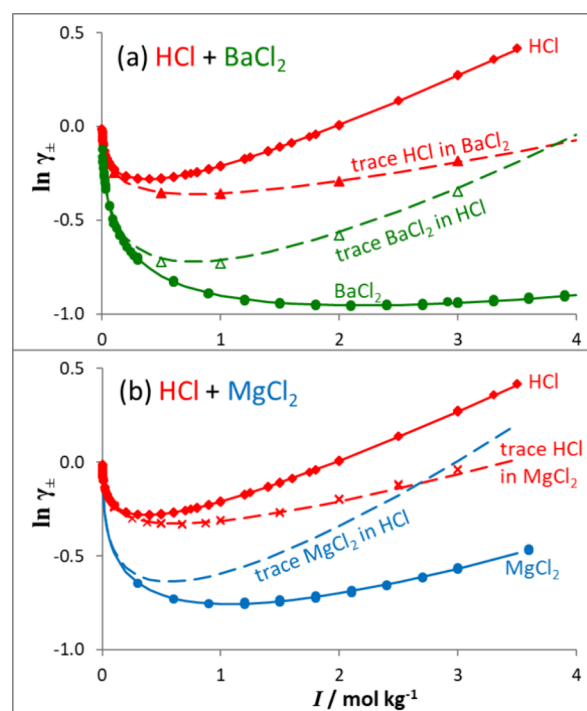


**Figure 2.** Algal growth in swimming pools is managed by controlling pH, which is defined by the activity of the hydrogen ion,  $\{\text{H}^+\}$ , not its concentration,  $[\text{H}^+]$ . ‘Dry-acids’ can be used to lower pH: the extent to which these acids dissociate and interact with other equilibria in solution is determined by a conditional equilibrium constant,  $K'$ , and the activity coefficients,  $\gamma$ , of the species involved in the reaction. Current thermodynamic models are unreliable because the  $\gamma$  depend on the concentrations of all the other species present in the solution, including those not involved in the reaction.

## THEORY

Certain linearities in  $\gamma_{\pm}$  and  $\Delta$  at moderate electrolyte concentrations are well-known<sup>39,45,58,59</sup> and obviously have a fundamental origin. (They are also exhibited<sup>24,60</sup> at intermediate concentrations by various independent properties such as volumes, heat capacities and even viscosity). Since many molecular-level causes are likely to be approximately colinear in this intermediate region,<sup>58,59</sup> hypothetical explanations abound, often supported solely by least-squares fitting. In contrast, the particular behaviors of  $\ln \gamma_{\pm}$  described by Harned’s rule (eq 1) are revealing. In addition to the remarkable overlap of trace curves illustrated for 1:1 systems

in Figure 1, highly distinctive patterns are exhibited by multivalent electrolyte mixtures as shown in Figure 3.

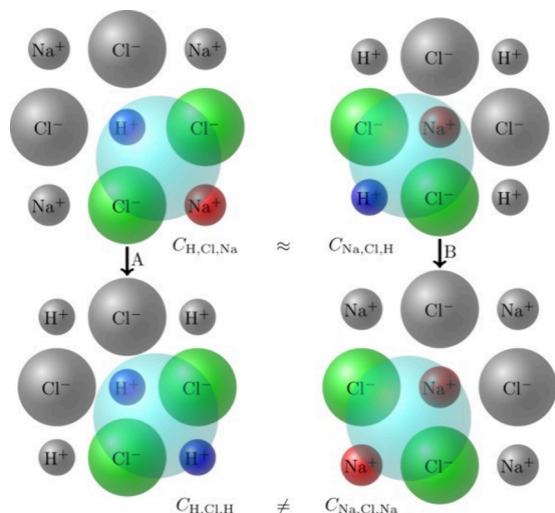


**Figure 3.** Mean ionic activity coefficients in aqueous mixtures of (a) HCl +  $\text{BaCl}_2$  and (b) HCl +  $\text{MgCl}_2$  showing the typical (1:1 + 1:2 electrolyte) intersecting curves calculated at trace concentrations (dashed curves) between those for the parent single strong electrolyte solutions (SSES, filled circles, and solid curves). Points (triangles or crosses) are the respective Harned equation extrapolations (eq 1) using electrolyte mixture data taken from the literature.<sup>23</sup>

**Ion Trio Concept.** As illustrated in Figure 4, ion trios in solution are molecular-level entities consisting of three ions formed from a statistical average over nearest neighbors interacting while under thermal motion. Such interactions happen even at low concentrations but they usually become predominant as DH coulombic attractions approach their asymptotic limit. Ion trios represent a collective phenomenon, which encompasses both electrostatic and structural effects. They provide a fundamental explanation for the distinctive patterns of  $\gamma_{\pm}$  in common ion mixtures as follows.

We propose that the overlapping trace curves in Figure 1 occur because the ion trios ( $\text{H}^+ - \text{Cl}^- - \text{Na}^+$  or  $\text{Na}^+ - \text{Cl}^- - \text{H}^+$ ) are essentially the same and the hydration and electrostatic characteristics of those three-ion groupings are necessarily nearly the same. Note that this equivalence occurs over a wide range of the medium’s concentration and despite the medium being otherwise different (pure NaCl for the trace HCl curve, and pure HCl for the trace NaCl curve).

For transitions from the mixed to the pure solution that take place at constant ionic strength (see, e.g., paths A or B in Figure 1 and Figure 4) we further propose that trios involving three ions ( $M-K-N$ ) are progressively replaced by trios with two identical ions (i.e.,  $M-K-M$  or  $N-K-N$ ). This ensures that  $\ln \gamma_{\pm}$  for either electrolyte changes linearly in accordance with Harned’s mixing rule (eq 1). Likewise,  $V^0$ , and  $C_p^0$  follow Young’s mixing rule (eqs 4 and 5).



**Figure 4.** Trio model for aqueous electrolytes at intermediate concentrations exemplified in 2-dimensions by ionic lattices for  $\text{H}^+$  (dark blue),  $\text{Na}^+$  (red) and  $\text{Cl}^-$  (green) and showing the **Figure 1** transition paths A (trace  $\text{H}^+$  in  $\text{NaCl}$  to pure  $\text{HCl}$ ) and B (trace  $\text{Na}^+$  in  $\text{HCl}$  to pure  $\text{NaCl}$ ) with the target ions  $\text{H}^+$  (at the center on the left) and  $\text{Na}^+$  (at the center on the right). Light blue ellipses show the trio interaction between the target ion at the center and, as a statistical average, just one  $\text{Cl}^-$  and one other cation.

For several reasons (SI), we envisage that the ion trios begin interacting as an ionic quasi-lattice assembles in aqueous solution. The three-body balance of attractive and repulsive forces determines the ISI and causes considerable variation in the slopes of  $\gamma_{\pm}$ ,  $\Phi$ ,  $V^{\circ}$ , and  $C_p^{\circ}$  versus concentration for different electrolytes. It is this combination of forces in ion trios that has been so theoretically elusive: (i) interion attractions and repulsions *both* operate simultaneously; and (ii) in three-ion mixtures at constant ionic strength, it is the common ion that controls the linear changes in  $\ln \gamma_{\pm}$ , *etc.* ostensible in the rules of Harned and of Young.

Above all, the mean ionic activity coefficients at trace concentration,  $\gamma_{\pm}^{\text{Tr}}$ , approach a clear, finite limiting value characteristic of one ion at infinite dilution immersed in an SSES (the pure aqueous solution of two other ions as one salt). That the profile of the ionic interaction over the whole range of concentration never vanishes (as an ion–ion association would do at infinite dilution of that ion), together with the net ion–ion repulsions indicated in many cases by  $\gamma_{\pm} > 1$ , are categoric proof of a dominantly electrostatic phenomenon. Models based only on ion *associations* are incapable of representing these general characteristics. They cannot predict  $\gamma_{\pm}^{\text{Tr}}$  accurately and they can only depict ion–ion repulsions by some numerical contortion.

**The Valence-Relation Convention.** The Valence-Relation Convention (V-RC) was formulated by Guggenheim in 1930<sup>8</sup> but it was later bypassed<sup>17</sup> and has since been overlooked. The V-RC applies generally to all SSES, which is the reason for its utility. It states (eq 2) that in any pure electrolyte,  $M_{\nu+}X_{\nu-}$ , which dissolves in water to yield the stoichiometric number  $\nu+$  of cations  $M^{z+}$  with charge  $z+$  and the stoichiometric number  $\nu-$  of anions  $X^{z-}$  with charge  $z-$ , and where  $\nu = \nu+ + \nu-$ :

$$[\gamma_+(M^{z+})]^{\nu+} = [\gamma_-(X^{z-})]^{\nu-} = [\gamma_{\pm}(MX)]^{\nu/2} \quad (2)$$

For 1:1 SSES, the V-RC holds that  $\gamma_+ = \gamma_- = \gamma_{\pm}$  throughout. Importantly, with the V-RC there is no assumption that  $\gamma_+$  or  $\gamma_-$  carry over to other solutions regardless of their composition, especially counterions. This is unlike either the MacInnes convention<sup>52</sup> or the IUPAC-adopted<sup>17,20</sup> B-GC based on  $\log \gamma_-(\text{Cl}^-) = -\mathcal{A}\sqrt{I}/(1 + 1.5\sqrt{I})$ . The V-RC is superior to those alternatives not because it is more accurate but because it is effective in practice. A successful convention, as judged ultimately by its wide adoption,<sup>61</sup> needs to be convenient, reasonable, and applicable without inconsistency across mixtures at all concentrations; judgements about accuracy are ill-considered because the *convention* is axiomatic even if its implementation leads to inconsistency (SI).

Our espousal of the V-RC specifies that eq 2 refers only to SSES or, equivalently, mixtures where all but one of the electrolytes present are at infinite dilution. Although SIACs have little to offer in the thermodynamic description of SSES (irrespective of convention), with electrolyte mixtures they are much more convenient<sup>37</sup> than  $\gamma_{\pm}$  and, critically, it is possible to *implement* the V-RC in mixtures without inconsistency.

Evaluating eq 1 for the measurable quantity  $\log \gamma_{\pm}(\text{MK})$  in the limit  $x \rightarrow 0$  fixes the value of the SIAC,  $\gamma_+(M^{z+})$ , at trace concentration through the standard relation eq 3 since the V-RC means that  $\gamma_-(K^{z-})$  is set by eq 2 and the SSES value of  $\gamma_{\pm}(\text{NK})$  at  $m_{\text{NK}}$ .

$$[\gamma_+(M^{z+})]^{\nu+} = [\gamma_{\pm}(\text{MK})]^{\nu} / [\gamma_-(K^{z-})]^{\nu-} \quad (3)$$

In other words, in the concentration limit where one ion approaches infinite dilution, its excess Gibbs energy depends only on that ion's individual properties and those of the (pure) electrolyte solution in which it is dissolved. This is analogous to the definition of other thermodynamic properties for species at infinite dilution in any particular solvent. The SIAC of an ion at trace concentration can thus be quantified precisely and unambiguously.

**Other Thermodynamic Properties of Common Ion Mixtures.** In addition to Harned's rule (eq 1), strong electrolytes at moderate concentrations are characterized by other general linearities. Both apparent molar volumes,  $V^{\circ}$ , (for solution density) and apparent molar heat capacities,  $C_p^{\circ}$ , exhibit such mixing behavior, known as Young's rule.<sup>62,63</sup> Young's rule holds that at constant pressure and temperature for a mixture of two electrolytes (A and B) with molalities,  $m_A$  and  $m_B$

$$V^{\circ} = (m_A V_A^{\circ} + m_B V_B^{\circ}) / (m_A + m_B) \quad (4)$$

$$C_p^{\circ} = (m_A C_{p,A}^{\circ} + m_B C_{p,B}^{\circ}) / (m_A + m_B) \quad (5)$$

where the subscripts denote the respective quantities for the parent electrolyte solutions at the same ionic strength. The validity of Young's rule continues to be evidenced by highly accurate modern measurements.<sup>64</sup>

In the same way as ion trios enable the rationalization of strong electrolyte mixing for changes in  $\log \gamma_{\pm}$  across constant concentration transects in accord with Harned's rule (eq 1), they also do so for  $V^{\circ}$  and  $C_p^{\circ}$  in accord with Young's rule. The exchange of one trio for another ( $M$ - $K$ - $N$  in the mixture by  $M$ - $K$ - $M$  or  $N$ - $K$ - $N$  from each SSES) ensures that these properties also transition in linear proportion to the ionic strength fraction. The only difference is that at each SSES boundary condition the volume and heat capacity contributions from the

ion at trace concentration tend to zero, unlike the finite limit approached by the excess Gibbs energy.

The simplicity of Young's rule means that the Trio model can represent volumes and heat capacities (SI) far more robustly than theoretical frameworks which depend entirely on the thermodynamic relationships linking them to activity coefficients. Since these orthogonal functions are in general sufficiently well characterized experimentally at 1 bar and 25 °C, it is better to treat them independently under these conditions. Only changes in volumes and heat capacities under other temperatures and pressures then need to be related through activity coefficients. Thus, far fewer adjustable parameters are required overall, facilitating more reliable extrapolations within the high-dimensional space of multi-component chemical systems.

**Modeling Aqueous Strong Electrolyte Solutions.** For all the reasons that have been outlined, a new approach to thermodynamic modeling of aquatic systems is needed.<sup>3,65</sup> In particular, the new framework must have a mathematical form known to describe accurately observed trends in the properties of single strong electrolyte solutions (SSES), it must use SIACs as a basis (together with a sensible convention), and it must be designed to describe mixtures canonically using functions constrained to capture known physical behaviors and prevent unrealistic extrapolations. The last requirement means that the modeling function's description of electrolyte mixtures must reproduce observed linearities such as the rules of Harned (eq 1) and of Young (eqs 4 and 5).

With SSES the extrapolation problem is generally controlled because there are plenty of experimental data (over just two dimensions); with mixtures, however, success hinges on how tightly the individual properties of every chemical species can be described. In this regard, any thermodynamically consistent model for mixtures must satisfy the general constraint called the Cross-Differentiation Relation (CDR)<sup>21,22,30,39</sup> shown in eq 6.

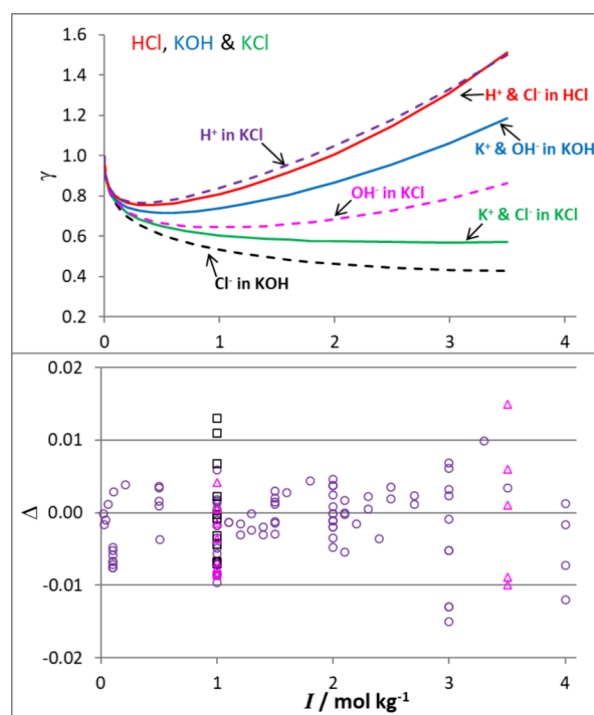
$$v_B \left( \frac{\partial \ln \gamma_B}{\partial m_C} \right)_{m_B} = v_C \left( \frac{\partial \ln \gamma_C}{\partial m_B} \right)_{m_C} \quad (6)$$

Accordingly, the function we use to represent SIACs combines the V-RC with a standard DH expression called the (extended) Hückel equation<sup>24,66–68</sup> but it is also explicitly designed to emulate Harned's rule and to satisfy the CDR. The SIAC for ion  $i$  in an SSES or three-ion mixture is given by eq 7:

$$\ln \gamma_i = \ln \gamma_i^{(DH)} + \sum_{j,k} c_{i,j,k} m_{j,k} + \sum_{j,k} \overline{D}_{i,j,k} m_{j,k}^2 \quad (7)$$

where  $j,k$  denotes a component electrolyte, with molality  $m_{j,k}$  which may or may not contain the target ion,  $i$ ;  $\ln \gamma_i^{(DH)}$  is a modified Debye–Hückel function that satisfies the CDR while allowing variable, so-called “ion size” parameters ( $b_{j,k}$ ) for different SSES;  $c_{i,j,k}$  are constants; and the  $\overline{D}_{i,j,k}$  in the quadratic term are functions of the electrolyte concentrations. Further details are given in the SI, where the rigor of this equation in modeling the activity coefficients and water activities of SSES and three-ion mixtures is demonstrated. Some representative results showing the function's ability to represent SIACs and the thermodynamic properties of three-ion mixtures are also shown in Figure 5.

To illustrate how the Harned's rule and the concept of ion trios are incorporated within eq 7, the SIAC for common ion  $K$



**Figure 5.** Top: individual behavior of ions expressed by their (V-RC defined) SIACs. The SIACs in three-ion mixtures of HCl(aq), KOH(aq) and KCl(aq) are calculated from  $\gamma_{\pm}^{\text{Tr}}$  and depend only on the standard relation eq 3, i.e., no modeling assumptions are invoked. At constant ionic strength, each ion's SIAC changes differently between the SSES (solid lines of red, blue and green respectively) and the mixtures at trace concentration (dashed lines for H<sup>+</sup> in KCl (purple), OH<sup>-</sup> in KCl (brown) and Cl<sup>-</sup> in KOH (black)). Bottom: Fit residuals,<sup>21,22,70–75</sup>  $\Delta = \gamma_{\pm, \text{meas}} - \gamma_{\pm, \text{calc}}$  found by the CDR-compliant Trio model (eq 7) for  $\gamma_{\pm}$ (KCl in KOH) as open squares,  $\gamma_{\pm}$ (KOH in KCl) as open triangles and  $\gamma_{\pm}$ (HCl in KCl) as open circles.

in the mixture MK + NK can be approximated using eq 8 for ionic strengths up to about 2 mol kg<sup>-1</sup>

$$\ln \gamma_K \cong -\mathcal{A} z_K^2 \sqrt{I} \left( \frac{\tau_{MK} \kappa_{K,M,K}}{1 + b_{MK} \sqrt{I}} + \frac{\tau_{NK} \kappa_{K,N,K}}{1 + b_{NK} \sqrt{I}} \right) + c_{K,M,K} m_{M,K} + c_{K,N,K} m_{N,K} \quad (8)$$

Here,  $\mathcal{A}$  is the DH limiting law slope;  $z_K$  is the ion charge;  $\tau_{MK} = 1 - \tau_{NK} = I_{MK}/I$  is the ionic strength fraction of MK;  $\kappa_{K,M,K}$  and  $\kappa_{K,N,K}$  are simple factors related to MK's and NK's stoichiometry (as defined in the SI, for equi-valent electrolytes, they are unity); and  $b_{MK}$  and  $b_{NK}$  are the SSES parameters. The value of  $c_{K,M,K}$  quantifies the interaction between the trio of ions K-M-K in one SSES, while  $c_{K,N,K}$  quantifies the interaction between the trio of ions K-N-K in the other. V-RC symmetry requires that each of these values is equal (or related in multivalent strong electrolytes) to the corresponding parameters of the ion trios M-K-M and N-K-N, respectively (hence  $c_{K,M,K} = c_{M,K,M}$  and  $c_{K,N,K} = c_{N,K,N}$  in 1:1 electrolytes). Equation 8 is a mathematical implementation (SI) of the Trio model's seminal assumption: at low concentrations, the log of the common-ion SIAC transitions between the two V-RC determined values of the parent SSES in linear proportion to the mixture's ionic strength fraction. Note,



though, that this assumption is not required at the boundary conditions, where the SIAC is fully defined.

While the common ion's SIAC is set by interpolation between the two SSES values, the noncommon ions are bound between one SSES and the trace curve limiting value (measured by extrapolating eq 1 to  $x = 0$ ). To about 2 mol kg<sup>-1</sup>, the SIAC for the noncommon ions is approximated by eq 9

$$\ln \gamma_M \cong \ln \gamma_M^{(DH,0)} + \ln \gamma_M^{(DH,mix)} + c_{M,M,K} m_{M,K} + c_{M,N,K} m_{N,K} \quad (9)$$

where  $\ln \gamma_M^{(DH,0)}$  is related to the DH term shown in eq 8, and  $\ln \gamma_M^{(DH,mix)}$  is a perturbation function formulated to ensure CDR conformance, as shown in the SI. The parameter  $c_{M,N,K}$  (which does not appear in eq 8 for the common ion) describes the interaction between the trio of ions  $M$ - $K$ - $N$ , and is expressed in the observed slope of the trace curve (Figure 1). The value of  $c_{M,N,K} \cong c_{N,M,K}$  (for mixtures of 1:1 electrolytes) reflects a statistical average of both coulombic and hydration effects due to the mixed ion trio as become apparent in Figures 1 and 3. Harned's rule is obeyed as long as the changes in the linear terms of eqs 8 and 9 are predominant.

For greater generality, certain second-order issues (*i.e.*, slight curvature of the SSES  $\gamma_{\pm}$  functions and limitations associated with Harned's rule known to arise at  $I > 2$  mol·kg<sup>-1</sup>) are addressed by the inclusion of the quadratic term in eq 7, where the functions  $D_{i,j,k}$  are also designed to satisfy the CDR (SI). Functions for  $V^{\ominus}$  and  $C_p^{\ominus}$  of individual ions are presented in the SI, for use with Young's rule (eqs 4 and 5), to obtain a full suite of mixture properties.

#### Modeling Chemically Reactive Aqueous Solutions.

Reliable activity coefficient values for the chemical species A, B, C, and D involved in the general chemical reaction  $A + B \leftrightarrow C + D$  are essential for quantitative modeling of multicomponent aquatic systems. Since the thermodynamic activity of any chemical species A, is described in terms of its concentration, [A], and the species activity coefficient,  $\gamma_A$ , by  $\{A\} = \gamma_A \times [A]$ , the conditional equilibrium constant,  $K'$ , applicable at finite concentration in solution (*i.e.*, under nonideal conditions when  $\gamma \neq 1$ ), is related to the equilibrium constant at infinite dilution,  $K^0$ , by eq 10

$$K' = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} = K^0 \times \left( \frac{\gamma_C \times \gamma_D}{\gamma_A \times \gamma_B} \right)^{-1} \quad (10)$$

In principle, values of  $K'$  in electrolyte solutions can be calculated from  $K^0$  using SIAC models; however, the use of eq 7 for this purpose is currently restricted because it applies to mixtures in which the ions derive from SSES. This precludes its use in describing conditional equilibrium constants where the  $K'$  being modeled necessarily includes activity coefficients for ions from weak electrolytes and for neutral species. To solve this problem (SI), the following variant, eq 11, can be used to correlate SIACs for ions present at trace concentration:

$$\ln \gamma_i^{Tr} = -\frac{\kappa_{i,j,k} \mathcal{A} z_i^2 \sqrt{I}}{1 + B\sqrt{I}} + C m_{j,k} + D m_{j,k}^2 \quad (11)$$

where  $z_i$  is the ion charge;  $\kappa_{i,j,k}$  is a constant specific to the stoichiometries of ion  $i$  and the electrolyte  $j, k$ ; and  $B, C$ , and  $D$  are three empirically determined constants. Equation 11 is rigorous (SI) only for mixtures at constant mole fraction composition but this is sufficient for modeling  $K'$  data for

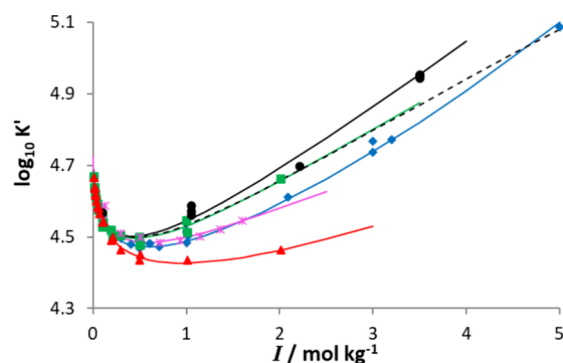
reactions occurring at trace concentrations in background electrolytes over a wide range of ionic strength. Values of  $B, C$ , and  $D$  are related to, but distinct from, those of the corresponding adjustable parameters in eq 7;  $c_{i,j,k}$  and  $C$  differ only because the  $\ln \gamma_i^{(DH)}$  and  $D_{i,j,k}$  functions are more complicated than the corresponding terms in eq 11.

## RESULTS

By applying eqs 7 and 11, the data for many electrolyte systems are described within reasonable uncertainty for numerous literature values taken from our JESS databases.<sup>23,67,69</sup> Good-quality fits are achieved in particular for:

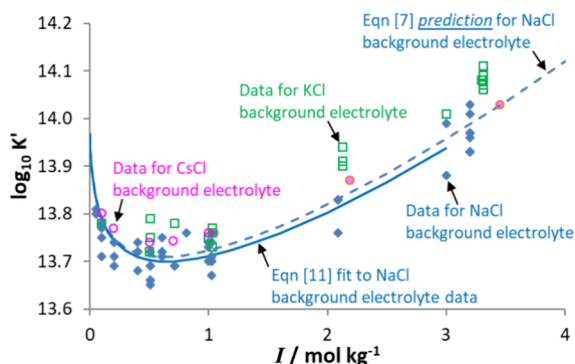
1. over 35,000 individual  $\gamma_{\pm}$ ,  $\emptyset$ ,  $V^{\ominus}$ , and  $C_p^{\ominus}$  data values for more than 200 SSES;
2. over 10,000 individual  $\gamma_{\pm}$ ,  $\emptyset$  and isopiestic data values for about 100 common-ion mixtures; and, as discussed in the next section below,
3. over 1,000  $K'$  measured for reactions in aqueous medium as a function of background salt concentration.

Representative subsets of these results at 1 bar and 25 °C with  $I \leq 5$  mol kg<sup>-1</sup>, including parameter values derived by numerical regression, are presented in the SI. Here, three highlights that illustrate the power of the Trio model are particularly worth mentioning. They are depicted in Figures 5–7.



**Figure 6.** Conditional equilibrium constants (as  $\log_{10} K'$ ) for the protonation of acetate ( $\text{CH}_3\text{COO}^-$ ) in electrolytes comprising NaCl (blue), KCl (green),  $\text{KNO}_3$  (pink), LiCl (red) and  $\text{NaClO}_4$  (black) showing measured values<sup>67</sup> (points) and eq 11 fits (solid lines), each with only 1 adjustable parameter value ( $C$ ) as described in the main text. The reactant species are, by experimental design, effectively held at trace levels. Current functions based on ionic strength only (dashed line) do not represent these ISI well.

First, adopting the V-RC produces SIAC values in common ion mixtures that are patently realistic. Figure 5 shows several three-ion mixtures in which, at constant ionic strength, each SIAC varies progressively between two well-defined limiting values. The common ion (*e.g.*,  $\text{Cl}^-$  in  $\text{KCl} + \text{HCl}$ , or  $\text{K}^+$  in  $\text{KCl} + \text{KOH}$ ) SIAC changes from one SSES value to the other. For the noncommon ions (*e.g.*,  $\text{K}^+$  and  $\text{H}^+$  in  $\text{KCl} + \text{HCl}$ , or  $\text{Cl}^-$  and  $\text{OH}^-$  in  $\text{KCl} + \text{KOH}$ ), each SIAC has one limiting value set by each ion's specific trace curve. In some cases, the trace SIAC lies between the two SSES curves ( $\text{OH}^-$  in  $\text{KCl} + \text{KOH}$ ), while in others it lies beyond them ( $\text{Cl}^-$  in  $\text{KCl} + \text{KOH}$ , or  $\text{H}^+$  in  $\text{KCl} + \text{HCl}$ ). The ion's identity and charge explicitly determine the SIAC's behavior in a given electrolyte medium. Note that in Figure 5, the cation and anion roles are interchangeable. Moreover, electroneutrality is maintained in



**Figure 7.** Conditional equilibrium constants (as  $\log_{10} K'$ ) for the water dissociation reaction,  $K' = 1/\{H^+\}\{OH^-\}$  as a function of ionic strength in aqueous NaCl (blue squares), CsCl (magenta filled circles), KCl (green squares), together with  $K'$  for CsCl(aq) by Harned and Schupp<sup>77</sup> (magenta empty circles). The CsCl & KCl data indicate the impact of ISI on this  $K'$ . Solid curve is eq 11 regressed to the  $K'$  reaction data measured<sup>67</sup> for NaCl. Dashed curve is a prediction made using the CDR-conforming Trio model (eq 7) (*i.e.*, without regression to the  $K'$  data). It derives from  $\gamma_{\pm}$  obtained in experiments where either HCl or NaOH are just diluted with NaCl.

the SIAC calculations so no approximation whatsoever is involved at the boundary conditions. The outcome is a much-improved ability to understand ISI trends, especially in  $\gamma_{\pm}$ .

Second, Figure 6 is an example of how conditional equilibrium constants can be represented precisely by eq 11. Other parametrized systems are given in the SI. We have found generally that the  $K'$  changes associated with increasing concentrations of different background electrolytes can be properly represented by SIACs for the individual species participating in any chemical reaction. A SIT-like<sup>39</sup> set of parameters (*i.e.*,  $C$  values with  $B = 1.5$  and  $D = 0.0$ ) has been determined for over 1,800 chemical reactions/species. Due to a serious paucity of measured values, the large majority of these parameter sets are for a function in ionic strength only. Nonetheless, the SI lists parameter sets for a number of systems measured at trace concentration in different background electrolytes, like the ones shown in Figure 6. A more precise description of SIAC changes in background electrolytes is thus possible but achievable less often than desirable (for now) because the available measured  $K'$  values are rarely sufficiently consistent (at  $I \geq 1 \text{ mol kg}^{-1}$ ) to justify more than 1 regressed parameter. Since the plethora of chemical reactions will never all be studied experimentally in a wide variety of background electrolytes, greater accuracy in thermodynamic modeling will require interaction parameters to be calculated by molecular simulations. Such calculations will be facilitated by the Trio model because it expresses a relatively simple three-body relationship. The relevant interactions should thus be a quantifiable outcome of electrostatics combined with the statistical average of separation distances, estimated, say, for any chemical species of interest by an uncomplicated molecular model (perhaps limited to closely bound water molecules).

Third, a special case involving water's dissociation reaction provides a check on the SIACs calculated for  $OH^-$ :  $\gamma_{OH^-}^{Tr}$  can be found independently by two methods. These are (a) using eq 7 to describe  $\gamma_{\pm}$  data measured for NaOH + NaCl mixtures as well as HCl + NaCl mixtures to obtain  $\{OH^-\}$  and  $\{H^+\}$ , respectively, and (b) the separate measurement<sup>76</sup> of conditional equilibrium constants,  $K'$ , for  $H^+$  and  $OH^-$  reacting in

the NaCl medium. The results are shown in Figure 7, with relevant calculations detailed in the SI; the agreement is excellent and well within experimental uncertainty.

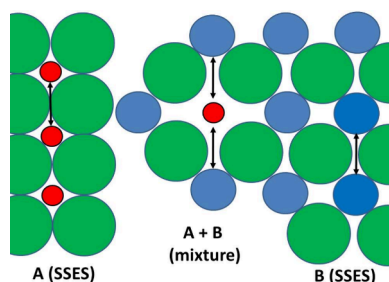
## DISCUSSION

There is clear utility in the good agreement achieved here between observed and calculated values but this does not prove the validity of eq 7. No modeling function can describe the full complexity of real chemical systems and the deceptive nature of numerical regression analyses is well-known.<sup>3</sup> Confidence in any proposed model becomes justified when it generates new explanations backed by quantitative observable predictions. (Values regurgitated from fits do not count.)

The broad and unifying features of eq 7 on the other hand are compelling. Designed compliance with the empirical eqs 2, 4, and 5 and explicit functional representation of the repulsive interactions that predominate at high electrolyte concentrations are both without precedent. So too is the same molecular-level explanation of electrolyte solution mixing for three orthogonal excess properties (Gibbs energy, volume, and heat capacity); at 1 bar and 25 °C our modeling functions consequently avoid unnecessary degrees of freedom needed to satisfy the thermodynamic relationships in concentration, pressure, and temperature. Additionally, the symmetry of ion trios means that just one parameter characterizes the two overlapping  $\gamma_{\pm}$  trace curves at very low ionic strengths and that value can be estimated from the “ion size” parameters of the two SSES. Compared to Pitzer, our correlations are simpler, equally precise, and require fewer adjustable parameters. Also, of utmost practical significance, eq 7 spawns a simple variant, eq 11, to describe conditional equilibrium constants,  $K'$ , which is analogous in form to the widely used SIT equation but has greater generality and precision.

Our ion trio proposition not only represents ion–ion repulsions explicitly but it also explains puzzling facts<sup>78,79</sup> about the role of cations in heats of strong electrolyte mixing which have stood unsolved for decades. Regardless of concentration, the enthalpy of mixing is often roughly independent of the anion.<sup>78–80</sup> This is true, in particular, of the enthalpy of mixing of two cations in the presence of a common anion.<sup>78,80</sup> Mixing of HCl or LiCl with NaCl or each other is significantly endothermic whereas mixing of HCl or LiCl with CsCl is exothermic to a similar or greater degree.<sup>78</sup> Young and co-workers<sup>78,79</sup> concluded that the largest heat effects were associated exclusively with the smaller cations. In terms of the Trio model, these observations imply that ion trio interactions are most pronounced when small cations are involved and that anion–cation–anion interactions are generally weaker than those of cation–anion–cation trios. A high charge-to-distance ratio would be expected to intensify ion–ion interactions. The fact that heat is evolved from mixtures when the cations have different ionic sizes can thus be rationalized by the Trio model (Figure 8), which suggests that the formation of the *mixed* trio reduces the amelioration of the primary cation–anion attractions. This causes the mixture to be stabilized relative to the SSES (*i.e.*, lower Gibbs energy): mixing is exothermic because the *primary* attractions in the mixture are increased. If cation–anion attractions were the only significant interaction, this observed evolution of heat upon the addition of a different cation would be difficult to explain. (Disrupting the molecular structure would usually be endothermic.) Note also that the observed correlations<sup>28</sup> between partial molar volume and heats of mixing (as well as





**Figure 8.** Stylized 2D representation of the quasi-lattice formed in two SSES and their common ion mixture when the cation is small (left), or is large (right), compared with one cation large and the other small (middle). The anion in common (filled green circles) is shown as being larger than the cations (blue filled circles and red filled circles) corresponding, for example, roughly to the ionic radii tabulated by Marcus<sup>81</sup> for  $\text{Cl}^-$  (181 pm),  $\text{Li}^+$  (69 pm), and  $\text{Na}^+$  (102 pm). On average, distances of approach (equal to the length of the double-headed black arrows) can be expected to be increased when a small cation exists in a lattice cavity created by the close-packing of two larger ions. If only attractive interactions were significant, this increased average separation would lead to an endothermic heat of mixing in contrast to the observed exothermic process which can be interpreted in terms of a reduction in ion trio repulsions.

between excess Gibbs energies and enthalpies) point to a common molecular-level explanation.

An especially valuable capability offered by eq 7 concerns the analysis of isopiestic data. In numerous strong electrolyte mixtures, particularly those of  $\text{HCl}(\text{aq})$  and  $\text{HBr}(\text{aq})$ ,  $\gamma_{\pm}$  for one component can be determined accurately by potentiometry but the characterization of the other electrolyte component depends, at best, on measured osmotic coefficients. McKay and Perring derived equations that calculate the activity coefficients of both electrolytes in a mixture from measurements of water activities.<sup>82</sup> Unfortunately, the indirect nature of their method (particularly in the numerical integrations required) means that it is subject to significant uncertainty. Elaborations on this (model independent) approach have been described<sup>83</sup> but they seem to pay insufficient attention to the problematic sensitivity of the numerical method. While direct measurements are obviously preferable, eq 7 provides a highly robust alternative: once the parent SSES are characterized, only two adjustable parameters are needed to describe *both* trace activity coefficient curves derived from isopiestic data for any three-ion strong electrolyte mixture at a given temperature. Moreover, if  $\gamma_{\pm}$  data for just one component electrolyte in a mixture is obtained, eq 7 allows calculation of the reciprocal trace activity coefficient curve as shown in Figure 3b for  $\text{HCl} + \text{MgCl}_2$ .

The most important insight from the Trio model presented here is that ion specific interactions are strongly characterized by each surrounding electrolyte in which the two electrolyte ions operate together on all other individual (charged) species. That ion trios arise even at very low concentrations is most evident in the effect of divalent salts like  $\text{MgCl}_2$  on the activity of  $\text{H}^+$ . One consequent implication is the prospect for a better definition of pH. Other advances can be expected, including the role ISI plays in Hofmeister series<sup>4,84</sup> and a greater surety in general speciation calculations. Improved solubility predictions would benefit the long-term quantification of both seawater acidification and carbon dioxide uptake.<sup>14,54,56,57</sup>

Well formulated, SIACs can help to interpret results and manage the combinatorial explosion of interactions arising from electrolyte pairings. They can also facilitate predictions. Carefully defined, SIAC changes in electrolyte mixtures are physically meaningful, ion specific, tightly constrained by thermodynamics, and not at all arbitrary (SI). As described here, they are furthermore in accord with the general empirical observations encapsulated by Harned's rule. Of particular practical value, a clear-cut and compatible description of SIACs can also be derived from conditional equilibrium constants,  $K'$ , measured for chemical reactions occurring at trace concentrations in "background" or "supporting" electrolyte solutions. This could enable, for example, measurements made with pH buffers to be aligned with one another to a much higher electrolyte concentration than is achievable at present.

Finally, these advances enable pH to be defined and quantified metrologically by adopting the V-RC and measuring the mean ionic activity coefficient,  $\gamma_{\pm}$ , of HX at trace concentration in any pure aqueous strong electrolyte MX. Since the activity of X is defined axiomatically in MX by the V-RC (eq 2), the activity of  $\text{H}^+$  is fixed algebraically at trace concentration (eq 3) without making any assumptions or modeling calculations. Given that the V-RC similarly defines the activity of  $\text{H}^+$  in HX, a measurement protocol based on an empirically justified linear interpolation (eq 1) between the two boundary values can also be specified to quantify pH at, say, ionic strength  $I = 1.0 \text{ mol kg}^{-1}$  in  $\text{HX} + \text{MX}$  mixtures. This proposed approach converges at  $I \leq 0.1 \text{ mol kg}^{-1}$  with the current definition of pH because at low concentrations all  $\gamma_{\pm}$  approach the same DH limiting values.

**Perspectives and Future Developments.** As noted above, it seems inevitable that computer simulations and statistical mechanics will be required to consummate ion trio parameter quantification by describing in general how pairwise attractions are progressively overwhelmed through the influence of a third ion in their vicinity. Such progress will possibly make use of the Ornstein–Zernike integral equation,<sup>85–88</sup> which enables the spatial correlations between ions in solution arising from the influence of intermediate ions to be calculated from the direct correlation between two ions. This calculation requires a closure relation to provide an additional equation or approximation linking either or both the total correlation function and the direct correlation function to the ionic interaction potential. Blum<sup>89–91</sup> and others<sup>85,92–96</sup> have investigated the use of various closure approaches including the generalized mean spherical approximation and hypernetted chain models but to date, these have produced neither consensus nor analytical solutions for practical applications at higher concentrations. It is reasonable to expect that the vexing theoretical complexities, which have so far thwarted these ideas<sup>97</sup> may be assisted by the present results because they show that three-ion interactions are predominant in aqueous electrolyte solutions roughly across the range  $1 < I < 5 \text{ mol kg}^{-1}$ .

Our overarching hope for this work is that it will dampen the disputation over SIACs (ref. 17 p. 168), which has dragged on in the literature ever since Lewis<sup>98</sup> introduced the concept in 1907. If this happens, significant theoretical and experimental benefits should follow. It is still occasionally necessary in science to cast doubt on intangible entities for reasons that are not just philosophical (e.g., ref. 99). Apart from addressing the confusion that often surrounds such matters, the question regarding single ion activities goes directly to the meaningful-

ness or otherwise of their definition, measurement, and possible uses.

The school of thought contending that SIACs can never be more than notional has had strong historical support from many distinguished thermodynamicists.<sup>8,21,43,52,100,101</sup> Reflecting Guggenheim's preeminent stature, his early position<sup>101</sup> has had a profound influence in dismissing single ion activities as having no physical reality and in rejecting any device to distinguish between activity coefficient values for different ions with the opposite charge. More recently, Malatesta<sup>102–107</sup> has been a prominent and penetratingly insightful critic of any suggestion that SIACs can be determined experimentally, regarding them as a mere artifact devoid of any genuine experimental validation.<sup>102</sup>

On the other hand, many other experts have inferred that ions have activities and activity coefficients just like neutral substances, implying that ions possess a distinct identity, each with its own individual properties. The review<sup>108</sup> of SIACs by Valiskó and Boda reflects this perspective, noting that it has been held by eminent scientists such as Lewis and Randall, Harned, and Brønsted (which is not to mention Hückel, Robinson, and Bates),<sup>66,109,110</sup> all of whom thought that individual ion activities were a natural and useful corollary of those for neutral chemical species. Debye–Hückel theory presupposes that SIACs exist and predicts individual ion values at low concentrations;<sup>24,48,61</sup> and, ratios of SIACs are unambiguously and thermodynamically defined in mixed electrolyte solutions.<sup>111</sup> Moreover, to deny SIACs is to deny liquid junction potentials,<sup>112</sup> which, in the light of much experimental and theoretical evidence, looks perverse.<sup>48</sup> Contrary to Guggenheim's injunction,<sup>113</sup> Robinson and Stokes<sup>22</sup> (p. 28) and others<sup>114</sup> go so far as to define the mean ionic activity coefficient of an electrolyte in terms of the SIACs instead of the other way around. Moreover, even Guggenheim (having initially emphasized the arbitrary nature of SIACs,<sup>43,101</sup>) seems eventually to have had second thoughts,<sup>113,115–117</sup> his reversal (in promulgating the Bates–Guggenheim convention<sup>17</sup>) drawing ironic comment.<sup>118</sup>

The literature on this subject of SIACs is thus in disarray, plagued in various ways by strong opinions and semantic imprecision. A regrettable feature of this coverage is that it is riddled with claims justified by “appeals to authority”, *i.e.*, statements attributed to famous experts in support of one position or another. Such arguments are generally made without proper context and against a backdrop of evolving and often incoherent ideas. Overhanging the subject of SIACs has thus been the nagging thought that if a supposed physicochemical quantity cannot be measured (as is being unconditionally stated of SIACs by IUPAC<sup>11</sup>), it is not real. However, other thermodynamic quantities that also only manifest as differences (such as enthalpy) are entirely respectable. In our opinion, those making the general case against SIACs (*e.g.*, ref 10) put insufficient weight on the axiomatic nature of thermodynamic conventions which are just needed to establish a numerical scale of values (SI).

Numerous reports claiming to measure SIACs experimentally have been particularly confounding. Significant numerical disparities<sup>111</sup> between experimentally derived values published for particular SIAC functions demonstrate just how chaotic they are. Hurlen *et al.*,<sup>119–124</sup> with keen awareness of the issues, have produced a large data set of “simple, coherent and reasonable” results but their method of calculating liquid junction potentials renders them inconclusive. Other less well-

founded measurements have been reported by various investigators,<sup>125–129</sup> including most often from the Vera research group.<sup>130–135</sup> Such attempts generally aim to minimize junction potentials (which is a reasonable objective) but, almost inevitably, rely on unconvincing assumptions.<sup>127,136–139</sup> The general omission (or dubious use<sup>124</sup>) of the word “convention” is especially noteworthy. There is a disturbing occurrence of least-squares regression fits to  $\gamma_{\pm}$  values purporting to be predictions.<sup>131–134,140</sup> The hazards in attempting to characterize SIACs without a well-defined anchor (in the form of a convention or of an explicit, consistent extra-thermodynamic assumption) were sadly illustrated when multiple sets of published SIAC values had to be rescinded by the authors<sup>130</sup> because the wrong sign globally had escaped detection!

An enticing prospect of the present work is the possibility of calculating accurate *changes* in junction potentials which might be tested through potentiometric titrations with liquid/solid-state contacts to various background electrolyte solutions at constant ionic strength. That the expected differences are unfortunately close to the current limits of experimental uncertainty is the main challenge. Such calculations may well involve comparisons between systems with more than three ions and, hence, may have to depend on additional assumptions such as the “cross-square rule”.<sup>80,141–144</sup> Work of both an experimental and theoretical nature to further explore these issues is underway.

## CONCLUSIONS

The concept of ion trios explains the general and distinctive patterns observed with strong electrolyte mixing, accounting most notably for (a) the strong electrolyte mixing rules of Harned and of Young; (b) the net ion–ion repulsions which often become predominant at higher concentrations; and, (c) the overlapping trace activity coefficient curves in three-ion univalent systems. Coulombic repulsions across cation–anion–cation trios are found to be especially consequential. Ion specific interactions, which have been so elusive, are revealed to be a straightforward consequence of attractive and repulsive electrostatic forces acting simultaneously. The Valence-Relation Convention, upon which the proposed pH definition and the Trio model are based, is easily implemented and it fixes SIAC values at each boundary condition unequivocally. As a result, the pH quantity can now be redefined without relying on theory. The highly constrained (CDR-conforming) Trio model can then be used to interpolate SIAC values robustly between these established limits over a wide range of concentrations, typically  $0 < I < 5$  mol kg<sup>-1</sup>. Reduced pH measurement uncertainty, of about an order of magnitude, can be expected. Changes in  $K'$  with increasing concentrations of different background electrolytes can be properly represented by SIACs for the individual species participating in any chemical reaction. In this way, secondary and tertiary pH standards can be established in closer alignment with the primary standard and with each other. These advances promise major improvements in the quantitative accuracy of thermodynamic modeling of multi-component aqueous systems. A demonstration program implementing the Trio model for 3 ion systems is available on request.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c07525>.

Representative results, supplementary details, mathematical framework of the Trio model, and literature references (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Peter M. May – Chemistry, School of MSCP, Murdoch University, Murdoch, WA 6150, Australia; [orcid.org/0000-0003-0434-3855](https://orcid.org/0000-0003-0434-3855); Email: [P.May@murdoch.edu.au](mailto:P.May@murdoch.edu.au)

### Author

Eric F. May – Fluid Science & Resources, School of Engineering, University of Western Australia, Crawley, WA 6009, Australia; Future Energy Export Cooperative Research Centre, Crawley, WA 6009, Australia; [orcid.org/0000-0001-5472-6921](https://orcid.org/0000-0001-5472-6921)

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsomega.4c07525>

### Author Contributions

Both authors are responsible for the whole work and have given approval to the final version of the manuscript. The authors contributed equally in development of the theory and in writing the manuscript. Ion trios were conceived by P.M.M. E.F.M. instigated the CDR conformance of the ion trio SIAC function.

### Funding

Murdoch University and the University of Western Australia provided operating support.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The name for ion trios was suggested by Heather May in a 2015 conversation with E.F.M. Darren Rowland helped prepare Figure 4. Informative discussions with colleagues over many years are greatly appreciated; Glenn Hefter (Murdoch University), Montserrat Filella (University of Geneva), Erich Königsberger (Murdoch University), and Darren Rowland (Murdoch University) are specifically acknowledged. Knowledgeable and thoughtful suggestions by (anonymous) reviewers, particularly concerning the comparison with approaches by statistical mechanics and problems with the experimental data for SIACs, were exceptionally constructive.

## ■ ABBREVIATIONS

B-GC, Bates–Guggenheim convention; CDR, cross-differentiation relation; DH, Debye–Hückel; IUPAC, International Union of Pure and Applied Chemistry; SIAC, single ion activity coefficient; ISI, ion specific interaction; SIT, specific ion–interaction theory; SI, Supporting Information; SSES, single strong electrolyte solution; V-RC, valence relation convention

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