



Volcano Plots Emerge from a Sea of Nonaqueous Solvents: The Law of Matching Water Affinities Extends to All Solvents

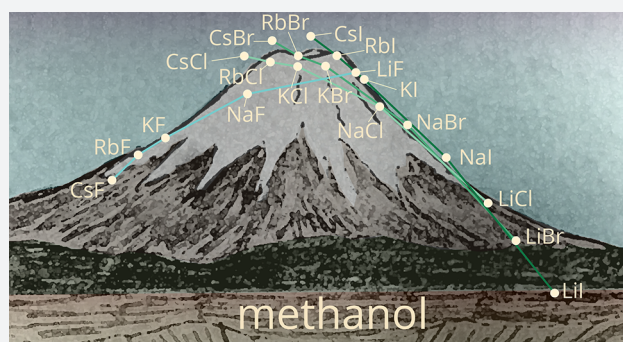
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Supporting Information

ABSTRACT: The properties of all electrolyte solutions, whether the solvent is aqueous or nonaqueous, are strongly dependent on the nature of the ions in solution. The consequences of these specific-ion effects are significant and manifest from biochemistry to battery technology. The “law of matching water affinities” (LMWA) has proven to be a powerful concept for understanding and predicting specific-ion effects in a wide range of systems, including the stability of proteins and colloids, solubility, the behavior of lipids, surfactants, and polyelectrolytes, and catalysis in water and ionic liquids. It provides a framework for considering how the ions of an electrolyte interact in manifestations of ion specificity and therefore represents a considerable conceptual advance on the

Hofmeister or lyotropic series in understanding specific-ion effects. Underpinning the development of the law of matching water affinities were efforts to interpret the so-called “volcano plots”. Volcano plots exhibit a stark inverted “V” shape trend for a range of electrolyte dependent solution properties when plotted against the difference in solvation energies of the ions that constitute the electrolyte. Here we test the hypothesis that volcano plots are also manifest in nonaqueous solvents in order to investigate whether the LMWA can be extended to nonaqueous solvents. First we examine the standard solvation energies of electrolytes in nonaqueous solvents for evidence of volcano trends and then extend this to include the solubility and the activity/osmotic coefficients of electrolytes, in order to explore real electrolyte concentrations. We find that with respect to the solvent volcano trends are universal, which brings into question the role of solvent affinity in the manifestation of specific-ion effects. We also show that the volcano trends are maintained when the ionic radii are used in place of the absolute solvation energies as the abscissa, thus showing that ion sizes, rather than the solvent affinities, fundamentally determine the manifestation of ion specificity. This leads us to propose that specific-ion effects across all solvents including water can be understood by considering the relative sizes of the anion and cation, provided the ions are spherical or tetrahedral. This is an extension of the LMWA to all solvents in which the “water affinity” is replaced with the relative size of the anion and cation.



INTRODUCTION

A great many biological and technology-related processes take place in solution, and nearly all such solutions contain electrolytes. Understanding the influence of electrolytes on solutions is therefore of utmost importance, both scientifically and economically.¹ However, the influence of ions on solution properties is complex.^{2–4}

The realization that the influence of electrolytes on solutions extends beyond the electrostatic charge, and that the individual nature of the ions is important, occurred in the 19th century,⁵ yet we are still working toward a quantitative theory capable of modeling and predicting the behavior of electrolyte solutions.^{6–8} This is partly because in the foundational theories of electrolytes, specific-ion effects were treated as the exception rather than the norm. That this is not the case has been clear for some time, but because of the complexity of the observed manifestations of ion specificity the origin of specific-ion effects is still debated.^{9,10} In the absence of a predictive general theory

of specific-ion effects, scientists and technologists who deal with electrolyte solutions rely mostly on empiricism, and on the general guidance of the Hofmeister and lyotropic series of electrolytes, despite an awareness that this series is frequently prone to exceptions.¹¹ The Hofmeister series orders ions based on the magnitude of their effect on several properties of aqueous solutions. Initially proposed for the effectiveness of salts in precipitating proteins out of solution, it has been found to apply in a great number of experiments. More recent experiments and investigations have shown that this series can reverse depending on a number of factors.^{3,12,13} It is important to recognize that the Hofmeister series is the *result* of the interplay of a number of interactions in solution. The term “Hofmeister effect” is frequently applied to observations of specific-ion effects in a manner that implies that because it is

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named it is understood, when in fact the series is empirical and the origin of the series is still debated. The term “Hofmeister series” is too often used as an explanation, masking our ignorance of the cause of these effects.

Understanding of specific-ion effects, and especially phenomena such as the reversal of the Hofmeister series, has benefited greatly from the empirical “law of matching water affinities” (LMWA), enunciated by Collins.¹⁴ This law predicts that, in aqueous solutions, ion pairs are formed by cations and anions with matching size (charge density). Collins explains that “the small ions of opposite charge form contact ion pairs because of electrostatic attraction; the large ions of opposite charge form contact ion pairs because this releases weakly hydrated water, which becomes strongly interacting water in bulk solution”.¹⁵ This is an extension of the “like seeks like” rule. Collins used “volcano plots” as one of the theoretical foundations for the LMWA. The term “volcano plot” arises from the shape of the plot which resembles a cinder cone in profile. Such plots were first published by Morris in response to a suggestion from Fajans, who first enunciated a “competition principle” regarding the dissolution of crystalline electrolytes and their interaction in solution.

Specific-ion effects are often interpreted as arising from the interaction of ions with water, but our recent investigation of ion specificity in nonaqueous solvents shows that universal ion-specific trends are observed across a wide range of solvents,¹¹ implying that ion-specific trends arise from the ions *independently* of the solvent (although the solvent mediates the magnitude of the effect). We recognize that the solvent matters as do interfaces, but these might be viewed as perturbations to the fundamental series that originates from the ions themselves, rather than the cause of the specific-ion effects observed. This leads us to the hypothesis that the LMWA arises from the ions themselves, rather than from their interaction with water or solvent. It is this hypothesis that we aim to test here. To this end we examine the relationship between volcano plots and the LMWA, and extend the volcano plot method to nonaqueous solvents, first in order to determine if volcano plot trends are manifest in nonaqueous solvents and second to test the arguments proposed to explain the LMWA. The analysis is intentionally qualitative, as the focus is on trends in specific-ion effects across a wide range of solvents, which, to the best of our knowledge, have not been previously explored.

■ RESULTS AND DISCUSSION

The Law of Matching Water Affinities. The volcano plots of Morris¹⁶ were cited by Collins¹⁴ as a thermodynamic foundation of his empirical “law of matching water affinities” (LMWA). The LMWA states that, in solution, oppositely charged ions (as well as charged groups) that have similar affinity for water spontaneously lose part of their hydration shells to associate and form a contact ion-pair (two ions interacting directly with no water molecules in between).

Collins built his argument on the volcano plots on thermodynamic observations such as the entropy of water molecules near an ion and on experimental evidence (viscosity *B*-coefficients, NMR, gel sieving chromatography, neutron and X-ray diffraction, etc.). Collins states that oppositely charged ions in solution tend to form contact (or “inner-sphere”) ion pairs when they have “matching water affinity”. Here *water affinity* refers to the strength of interaction of the ion or charged moiety with water, and can be expressed via a range of

properties of ions in solution. For volcano plots, Collins uses the absolute Gibbs free energy of hydration of the gaseous ion as a measure of its affinity for water. The water affinity is directly related to the charge density on the ion (which is proportional to size for spherical monatomic ions). The smaller the ion, the greater the charge density. Collins argued that ions tend to associate when their interactions are stronger than their interaction with water (they are both small) or when their interaction with water is less favorable than the water–water interaction (when both ions are large). Ions with comparable (“matched”) hydration enthalpies or free energies form salts that are the least soluble. It is argued that this is because ions with matched charge densities have comparable interactions with water and tend to form inner-sphere ion pairs in solution. Therefore, according to Collins, charged and also noncharged moieties in solution will prefer to associate with moieties of matching absolute free energies of hydration. This is an extension of the “like dissolves like” principle. This framework has proved successful for rationalizing a variety of observations, such as ion pumps, the interactions of ions with proteins, and ion selectivity in ion exchange chromatography.

The LMWA was restated and expanded in four subsequent papers.^{15,17–19} After the publication of the LMWA, “volcano plots” and the LMWA are cited indistinguishably. A similar “like seeks like” principle has been formulated by Lyklema when reviewing specific-ion effects on the stability of colloids: small cations are more effective at destabilizing colloids that have small negatively charged surface sites (i.e., Li^+ is more effective than Rb^+ in precipitating TiO_2 , with surface sites of deprotonated hydroxyl groups) and vice versa (AgI colloids are precipitated at lower concentrations of RbI than LiI).²⁰ An older and analogous concept is the hard–soft principle of acids and bases (HSAB).²¹ This states that “hard” (nonpolarizable) acids prefer to bind to “hard” bases, and “soft” (polarizable) acids prefer to bind to “soft” bases. This influences a large number of phenomena in solution, such as the rates of nucleophilic substitution reactions and the formation and stabilization of metal–ligand complexes.²¹

The LMWA concept has found resonance with the scientific community. The papers introducing the LMWA^{14,15,17–19} have had a large impact in fields spanning (bio)chemistry and (bio)physics to pharmacology, physiology, food science, materials science, polymer science, and microbiology. There is no doubt that the LMWA has advanced understanding of specific-ion effects both experimentally and theoretically, as recognized by many authors.^{6,22,23}

Limitations of the LMWA. The intuition built into the LMWA is formidable, but it is a simplistic model with intrinsic limitations.^{4,24,25} As such, it is important that the shortcomings and inconsistencies are acknowledged if a predictive understanding of the behavior of ions and charged sites in solution is to be achieved.

A number of authors have pointed out weaknesses in the foundations of the LMWA. The first criticism is the usage of volcano plots to explain ion–ion interactions in solution. The quantities plotted on the volcano plots are standard thermodynamic quantities. As such they refer to ions at infinite dilution, and hence the application to ion–ion interactions is tenuous. The connection between the two physical situations of infinite dilution and finite concentrations has not been justified. An additional incongruence is the explanation for the interaction between large ions in solution. The justification for the LMWA assumes that the interactions

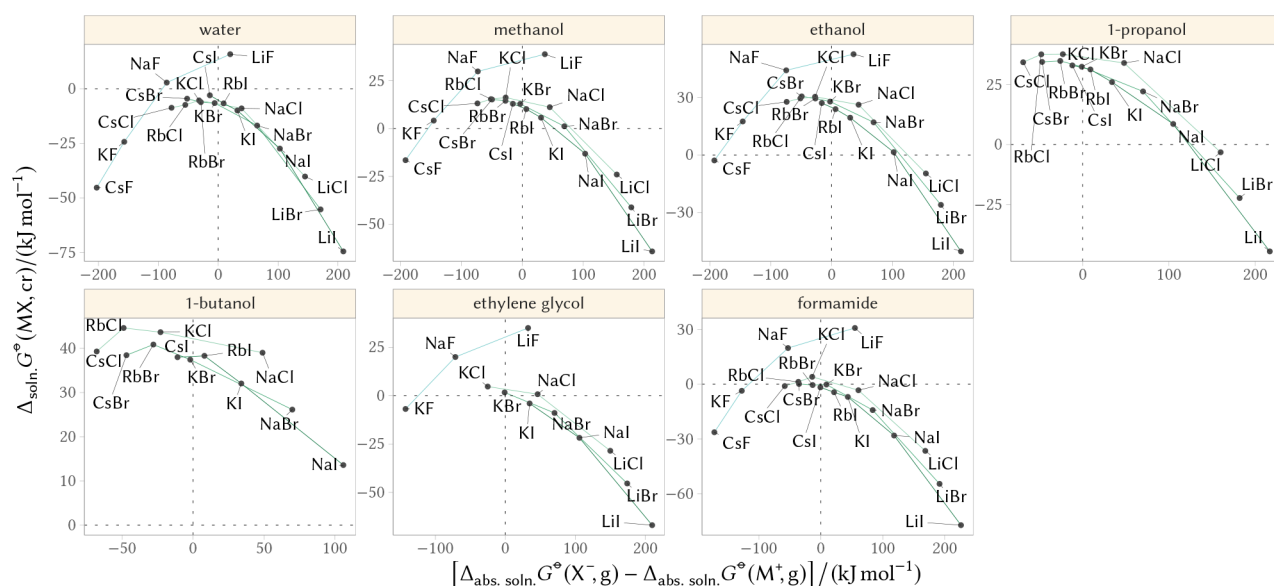


Figure 1. Gibbs free energy of dissolution of salts versus the difference in the absolute free energies of solvation of the constituent ions for a range of protic solvents. Colored lines are drawn to help identify the cation trends (constant anion).

between large ions and water are less favorable than water–water interactions; however, the hydration energy of large ions is large and favorable (negative), and therefore this argument cannot be sustained. Large ions must be preferentially interacting for another reason, most likely due to attractive dispersion forces.

These observations were first made by Lo Nostro and Ninham,²⁶ and reiterated and expanded by Duignan et al.,²⁷ who proposed a different volcano plot based on the *B*-coefficients from Bromley’s theory²⁸ (not to be confused with the Jones-Dole viscosity *B*-coefficient *B_v*). They obtained a “reversed volcano” with a clearer physical meaning than the explanations behind the LMWA. Salis and Ninham⁹ attempted a reconciliation of the quantitative and qualitative views, as the theoretical basis for the LMWA is questionable but its predictions are correct; however, as yet, the quantitative theoretical approach proposed by Ninham and collaborators has not been as broadly received. They argue that a theory that correctly treats electrostatics and quantum mechanical dispersion forces can quantitatively predict the behavior and association of both charged and noncharged ions and sites in solution. This theory develops a wider framework which includes interactions between ions and uncharged surfaces, in which the LMWA is contained as a subcase. They propose that small ions prefer to lose water molecules and interact directly as the small size gives rise to large interaction energies (in agreement with the LMWA), whereas large ions interact strongly by dispersion forces (in contrast to the LMWA which has these ions interacting weakly). When ions of different sizes interact, neither dispersion forces nor electrostatic interactions are highly favorable. The latter argument also explains the adsorption of large ions onto uncharged surfaces and uncharged protein moieties by means of dispersion interactions.

Definition of a Volcano Plot. We wish to clarify how we define a volcano plot. The term volcano plot refers to a scatter plot where the data trend follows an overturned “V”: it monotonically increases in a linear (the adjective is loosely applied) fashion up to a maximum, and then decreases, monotonically and linearly, with a slope of similar absolute

value to the ascending section. Here we recognize a volcano trend when two conditions are met. First, a scatter plot of a particular property of an electrolyte shows a maximum with respect to the difference in a particular property of the anions and cations making up the electrolyte. This may for example be the difference in size. Second, the peak of the volcano (i.e., the maximum) for different series occurs in a quite narrow interval of values of the difference. The plot is therefore quite symmetrical with respect to a vertical axis that goes through the maximum, thus resembling the shape of a volcanic cinder cone in profile. When evaluating volcano plots formed from electrolytes, the trend can be observed with a common cation for a number of anions (anion trend) or with a common anion and a number of cations (cation trend).

Our interest is in specific-ion effects in different solvents. We have previously looked at the specific-ion trends of several properties of solutions and their dependence on nonaqueous solvents.^{11,29} We are now interested in determining if volcano plots are evidenced in nonaqueous solvents, noting that volcano plots have been used to explain the LMWA which implies water is the solvent and that water is inherent to observation of the volcano trend. Should volcano trends be evident in nonaqueous solvents, we wish to determine if they show the same trends as those observed in aqueous solvents. In order to do this, we have inspected a number of electrolyte solution properties (*y*-axis) against the difference of a property of the constituting ions (*x*-axis).

There are opposing interpretations of volcano plots. One interpretation places interactions of the ions with the solvent at the center, attributing the volcano trend to the ion–solvent interaction, represented by the solvation energy.^{14–19,23} Alternatively, volcano plots are attributed to the characteristics of the ions (i.e., size, associated polarizability, surface charge density, etc.).^{30,31} In the first case, we would expect to see the volcano plots to be altered significantly by the solvent. Also, the volcano plots should be observed for polyatomic anions with nonspherical symmetry (such as thiocyanate and acetate).

Classic Volcano Plots. We have extended the “classic” treatment of volcano plots performed by Morris to nonaqueous solvents. This consists of plotting the standard

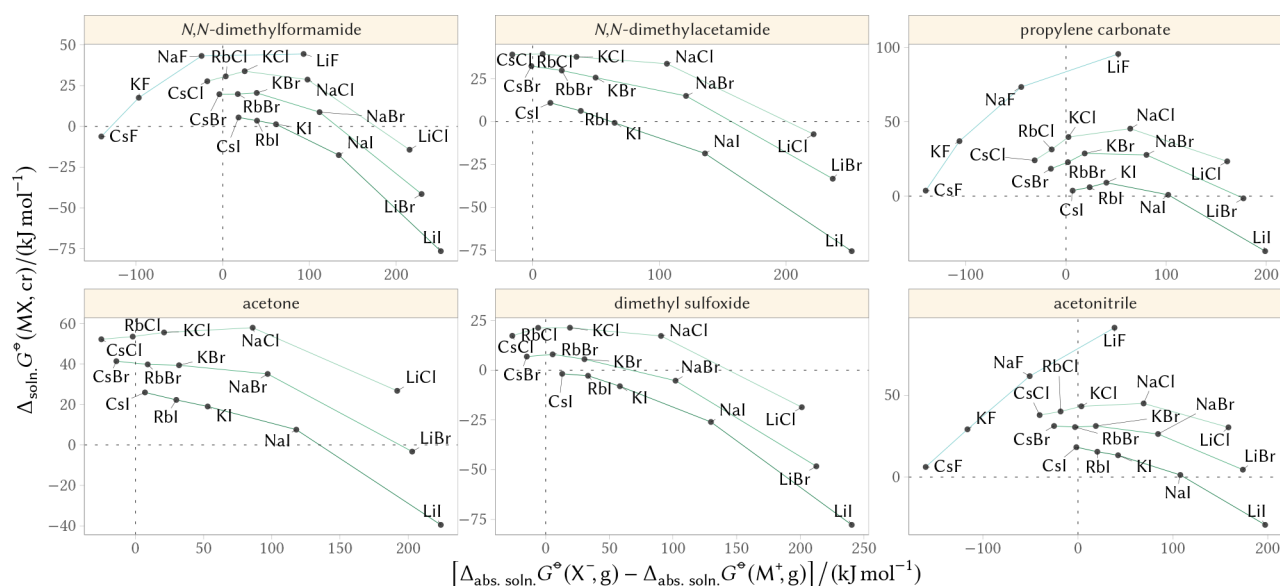


Figure 2. Gibbs free energy of dissolution of salts versus the difference in the absolute free energies of solvation of the constituent ions for a range of aprotic solvents. Colored lines are drawn to help identify the cation trends (constant anion).

enthalpy $\Delta_{\text{soln.}}H^\ominus$ (or Gibbs free energy $\Delta_{\text{soln.}}G^\ominus$) of dissolution of a crystalline salt versus the difference in absolute solvation enthalpies $\Delta_{\text{abs. soln.}}H^\ominus$ (or Gibbs free energies $\Delta_{\text{abs. soln.}}G^\ominus$) of the gaseous ions composing the salt. The data sources are listed in the Supporting Information, p S3. The relationship among these quantities is shown as a Born–Haber cycle in the Supporting Information, Figure S1. Starting with the alkali metal halides, the Gibbs free energies and the enthalpies of dissolution of the crystalline salt are presented versus the difference in the absolute Gibbs free energies and enthalpies of solvation of the constituent ions. Figures 1 and 2 show, for alkali metal halides, the Gibbs free energy of dissolution of the salt versus the difference in the absolute Gibbs free energies of solvation of the constituent ions for a range of solvents, where the lines follow the cation trends (constant anion). Figure S6 and Figure S7 of the Supporting Information show the analogous plots for the enthalpies.

The volcano trend is maintained across *protic* nonaqueous solvents, the only apparent influence of the solvent being a shift in the y -axis. Notably the shift in the y -axis shows a definite trend across the alcohols from methanol to butanol, whereas the data for ethylene glycol and formamide are similar to water.

This demonstrates that, for bulk standard thermodynamic properties, the same trends arise in *protic* solvents as in water, showing that the phenomenon is *not exclusive* to water. This is all the more surprising as the properties of these solvents differ substantially, in particular, their relative ability to solvate anions (see Table 1). The interaction strength of cations with the solvent is quantified by the Gutmann donor number, DN, and the interaction strength of anions with the solvent is quantified by the Gutmann–Mayer acceptor number, AN. In both cases larger numbers indicate stronger solvation. It is apparent that the Gibbs free energy of transfer $\Delta_{\text{transfer}}G^\ominus$ is small between the solvents ethylene glycol, formamide, and water (all three solvents have a structured hydrogen bonding network), whereas $\Delta_{\text{transfer}}G^\ominus$ becomes greater for the alcohols as the hydrophobicity and size of the solvent molecules increase.

Table 1. Some Properties of the Solvents Related to the Solvation of Ions^a

solvent	DN	AN	α	H bonding
water	18	54.8	1.17	3D H-bonded
ethylene glycol	20	43.4	0.9	highly structured
methanol	30	41.5	0.98	linear H-bonded
formamide	24	39.8	0.71	highly structured
ethanol	32	37.1	0.86	linear H-bonded
<i>i</i> -butanol	37.0	35.5	0.79	protic
1-propanol	30	33.7	0.84	linear H-bonded
2-propanol	36	33.5	0.76	linear H-bonded
1-butanol	29.0	32.2	0.84	linear H-bonded
<i>N</i> -methylformamide	27	32.1	0.62	linear H-bonded
pentanol	25.0	31.0	0.84	linear H-bonded
<i>i</i> -pentanol	32.0		0.84	protic
2-butanol		30.5	0.69	protic
<i>N</i> -methylacetamide		23.7	0.47	linear H-bonded
nitromethane	2.7	20.5	0.22	aprotic
dimethyl sulfoxide	29.8	19.3	0.00	aprotic
sulfolane	14.8	19.2	0.00	aprotic
acetonitrile	32	18.9	0.19	aprotic
propylene carbonate	15.1	18.3	0.00	aprotic
ethylene carbonate	16.4		0.00	aprotic
<i>N,N</i> -dimethylformamide	26.6	16	0.00	aprotic
<i>N,N</i> -dimethylacetamide	27.8	13.6	0.00	aprotic
acetone	17	12.5	0.08	aprotic

^aDN is the electron pair donicity (Gutmann donor number), with units kcal mol⁻¹; AN (Gutmann–Mayer acceptor number) and α (Kamlet–Taft) the net hydrogen bond donicity. Values from Marcus,³² solvent hydrogen bonding from Jenkins and Marcus.³³

In aprotic solvents, for *cations* (constant anion), the volcano trend is maintained, but the peak position is shifted toward positive x -values, and the “arms” corresponding to the different cation series are vertically displaced. This indicates a substantial difference in solvation between iodide, bromide, and chloride. That is, the *protic* solvents seem to be equally good solvents for monovalent anions, with the exception of fluoride which is poorly solvated, but aprotic solvents

differentiate between the anions such that the solvation is ordered: iodide > bromide > chloride > fluoride. Small anions (Cl^- , F^-) or anions containing a localized negative charge on the oxygen atom (CH_3COO^-) are good hydrogen-bond acceptors and therefore are strongly solvated in protic solvents (high AN, see Table 1), but are weakly solvated in aprotic solvents. In contrast, large anions such as I^- and ClO_4^- , that are weak hydrogen-bond acceptors, can also be solvated through dispersion interactions in aprotic solvents, and therefore the difference in solvation energies between protic and aprotic solvents is not as large.³⁴ The enhanced reactivity of anions in nonaqueous solvents, derived from their poor degree of solvation (“naked” anions) is advantageous in several organic synthesis reactions.³⁵

Whereas the *anion* (constant cation) trends for protic solvents follow the volcano trend (see the Supporting Information, Figure S31 and Figure S33), the volcano shape is lost in aprotic solvents; see the Supporting Information, Figure S32 and Figure S34. As the data regarding fluoride salts are not available in aprotic solvents, it is not possible to observe the complete trend. From these observations, some general rules of thumb can be proposed. First, the specific-ion trends observed in water are observed in protic solvents. Second, in aprotic solvents the specific-ion trends observed in water are likely to hold for the cation trends (constant anion) but not for the anions (constant cation).

For anion trends in particular, it often happens that the electrolyte occupying the peak position of the volcano changes, when changing from one solvent to another. This has been reported by Arslanargin et al.³⁶ for the dissolution enthalpies of the potassium fluoride–chloride–bromide series in water and propylene carbonate: it increases from fluoride to bromide in water, whereas it decreases from fluoride to bromide in propylene carbonate. The larger data set used here shows that this is exhibited across all solvents including protic solvents (e.g., in propanol).

The observed volcano shape for the enthalpies of dissolution of anions can be justified as follows: in aprotic solvents, the enthalpy of dissolution of anions gets less favorable (more endothermic, and therefore more positive) as the anion size decreases with respect to the cation size, because the dispersion contributions to the ion–solvent interactions become smaller. An “exploded” volcano plot of enthalpies is shown in Figure S8 and Figure S9 of the Supporting Information, to facilitate the analysis of the single anion trends for different cations. As anions are quite polarizable, the dispersion interactions play an important role in their solvation. This increasing dissolution enthalpy with decreasing anion size gives rise to the “right arm” of the volcano. The solvation of the anion becomes more favorable only when specific bonding interactions with the solvent, such as hydrogen bonds, intervene. These interactions are what gives rise to the left slope of the volcano, which is not observed if the solvent is incapable of these interactions. Therefore, a true volcano shape is only going to be observed for protic solvents, which can hydrogen-bond and are therefore good anion solvators,³⁷ or in cases where the solvent can form specific interactions with the anion.

The presence of common trends across solvents has been noted on occasion before, for instance, by Criss and Mastroianni,³⁸ who analyzed the cationic viscosity *B*-coefficient in water, methanol, and acetonitrile, and also inferred that water is not a unique solvent with regard to interactions with

ions. However, further experimental work is required in order to determine the specificity of the solvent influence at finite concentrations.

■ INTERPRETATION OF VOLCANO PLOTS IN NONAQUEOUS SOLVENTS

Origin of Volcano Plots. Some authors^{14–19,23} attribute the origin of the volcano trend to the interactions of the ions with the solvent, following the original idea of Fajans’s competition principle.³⁹ Other authors instead see it as a consequence of the properties of the ions alone, such as size.^{30,31} In an attempt to clarify the situation, two tests are performed here.

First, we can use the difference of the radii of the ions composing the electrolyte in place of the difference of their absolute solvation energies. As can be seen in plots S10–S13 (cation trends) and S35–S38 (anion trends) in the Supporting Information, the same volcano trend is obtained. It must be highlighted here that the ionic radii used in the plots are those for the ions in *water*, as this is the only solvent for which estimates of the solvated ion sizes are available. In a different solvent, these are likely to be different, as they depend on the ion coordination number, which changes across solvents.⁴⁰ But these aqueous radii correlate well with the *ab initio* radii calculated by Parsons and Ninham,⁴¹ and they are available for a larger number of ions than the *ab initio* radii. The aqueous radii values provide an estimate that is sufficient for nonaqueous solvated ions, especially as the cation–anion difference has been used and its trend can be expected to vary even less than the absolute values of the individual radii.

As the volcano shapes are retained when using the differences in the ionic radii in place of the ionic solvation energies difference, the hypothesis that it is the properties of the ions alone that give rise to the volcano trend appears equally valid. Moreover as the radii are a more fundamental characteristic, it can be argued that the radii are ultimately the origin of the volcano trend. Fajans and Johnson³⁹ argued that the solvation enthalpies rather than radii are the best measure because the maximum of the volcano occurs when the former is closer to zero. This was also used to justify the “matching solvent affinity” idea and the competition principle itself. But the maximum is not at zero in all solvents represented in Figure 1 and Figure 2. In addition, the fact that the maxima occur at nonzero radii differences (Figures S10–S13) can be interpreted as a solvent-specific characteristic, as the region of the solvent that most strongly interacts with the ion will differ for cations and anions (i.e., for a certain solvent with anion-solvating and cation-solvating groups of a certain size, ions will be best solvated when their size difference is closest to the difference in distances of solvation of the anion and cation). The position of the maximum therefore reflects the asymmetry of the solvent molecules. This could be further tested by estimating the solvated radii of ions in nonaqueous solvents.

A second test that can be made is to look at the trends for electrolytes containing polyatomic ions of different geometries: tetrahedral, such as ClO_4^- and NH_4^+ , trigonal planar (NO_3^-), linear (SCN^-). For polyatomic ions the ion is not spherical, and therefore the radius of the ion is a poorly defined measure. Therefore, for polyatomic ions, plots against the difference in radii of the anion and cation are less likely to show a volcano trend, whereas plots against the differences in enthalpy or Gibbs free energy of solvation should still exhibit a volcano trend, if the origin of the volcano trend is truly the energetics

of the interaction of the ions with the solvent, as these measures remain reliable for polyatomic ions. However, for polyatomic ions, volcano plots are generally not observed, either when the solvation energies or the radii are used to construct the x -coordinate (abscissa). Exceptions are electrolytes containing ions with tetrahedral geometry, such as perchlorates and ammonium salts, which do show an extremal behavior that is in accordance with a volcano plot. Volcano plots of electrolytes containing an alkali metal cation and a polyatomic anion are shown in the Supporting Information, Figures S15–S18 (connecting lines highlighting cation trends). In addition, electrolytes containing a tetralkylammonium cation are plotted in Figures S21–S28 (cation trends) and Figures S41–S48 (anion trends). Although not all electrolytes are available, there is little evidence of a volcano trend in both cases.

The above two tests indicate that the radii hypothesis is preferable over the solvation energies hypothesis, as they give equal results in terms of volcano plots, and the former is a simpler, more fundamental concept. Further, volcano trends are not observed for most salts containing polyatomic ions, whereas they would be expected under the solvation energies hypothesis. Finally and importantly, the solvation energies depend on the size of the ion. It is important to clarify here that when the effect is attributed to the “radius” or “size” of the ion, all other properties of the ion that are convoluted with size (polarizability, etc.) are included. If the volcano plot can truly be ascribed to the ion alone, then it would be most interesting to acquire the solvated radii of ions in nonaqueous solvents. Using these radii, an analysis of the position of the maximum in volcano plots in different solvents might reveal important details of solvation such as the distance of solvation of ions in different solvents and differences between cations and anions.

Details about the Trends of Polyatomic Ions. Volcano plots of electrolytes containing polyatomic anions are shown in Supporting Information, Figures S15–S18 (cation trends). The perchlorates show extremal behavior and are therefore in agreement with a volcano trend. The maximum for these series is not positioned close to a zero x -value as occurs in the classic volcano plots of alkali metal halides, but is shifted toward positive values. Plots against the difference in solvation energies and against the difference in radii show the same trend, thus indicating no preferential dependence of the volcano on solvation energies rather than radii. For thiocyanates, formates, and acetates, too little data are available to make an assessment, but the data are plotted for completeness.

For polyatomic cations (alkylammonium and ammonium cations), plots are reported in the Supporting Information, Figures S21–S28 (cation trends) and in Figures S41–S48 (anion trends). With the exception of ammonium electrolytes, no volcanoes are observed for the cation trends in the classic volcano plots for enthalpy (Figures S21 and S22), whereas when the radii are used in the x -axis, trends that could be in better agreement with the volcano emerge in protic solvents (Figure S25), but not for aprotic solvents, as shown by Figure S26. The same observations are valid for the Gibbs free energies plots (Figure S23 and S24, Figures S27 and S28). The anion trends are difficult to assign, but cannot generally be held to be in agreement with volcano plots for the enthalpies of polyatomic cations halides, both in protic and aprotic solvents (Figure S41 and S42), and again no substantial difference is obtained by plotting the difference of the enthalpies of solution

of the ions or the difference of the ionic radii on the abscissae (radii plotted in Figures S45 and S46). Volcano trends appear for the Gibbs free energies of polyatomic cations paired with halides in protic solvents (Figure S43 and Figure S47), but do not in aprotic solvents (Figure S44 and Figure S48). Overall, too little data are available to assess the trends for polyatomic cations that are paired with polyatomic anions, but the data are shown for completeness.

Consequences. As espoused in the section **Classic Volcano Plots**, the existence of volcano plots in other solvents infers that, across solvents, the ion-specific trends observed in water will be observed in other protic nonaqueous solvents, and that the trends observed in water are more likely to hold for cations in nonaqueous solvents than for anions. This poses questions about the role of the solvent (hydrogen bonding, polarizability) in anion solvation.

The trends in standard solution thermodynamic quantities behave differently than the electrostriction trends discussed in our previous work,²⁹ despite both being bulk properties of solutions. For electrostrictive volumes, we have seen that both cations and anions follow the same ion-specific series across all solvents. Here, the homogeneity in ion-specific behavior holds for cations in protic and aprotic solvents and anions in protic solvents, but not for anions in aprotic solvents. That is the ion-specific behavior of anions in aprotic solvents are solvent dependent. How do the two results reconcile? Despite solution energies and electrostrictive volumes being both bulk properties at standard concentration, they are very different in nature, with the first being more sensitive to ion–solvent specific interactions. This also shows that experiments can probe different aspects of ion–solvent interaction, and therefore the series observed can reveal different details of solvation.

This information is also useful in terms of predicting the unknown ion-specific trends in nonaqueous solvents where the corresponding trends are known in water. It must be stressed here that all of the above analysis and observations are valid for *standard, bulk* quantities. We explore whether this holds at real concentrations below.

■ VOLCANO PLOTS IN THE “REAL WORLD”

As stated in section **Limitations of the LMWA**, in the foundation of the LMWA, standard thermodynamic quantities were used to explain electrolyte behavior at finite concentrations. Arguments that use ion–ion interactions to explain data at infinite dilution are questionable, as the activity of a species at infinite dilution is by definition 1, and therefore ion pairing is excluded. Despite this, the LMWA holds very well in water and explains a number of phenomena that occur in solution at finite concentrations of electrolyte (and often in very complex systems, where surfaces, macromolecules, high concentrations, and so on are present). The quantities analyzed so far contain no information about the behavior of ions at real concentrations (but still they are useful in informing the ion–solvent interactions in nonaqueous solvents!). An attempt at investigating the volcano trends at finite concentrations in water and nonaqueous solvents is therefore made here, by considering the solubility and activity coefficients of electrolytes in nonaqueous solvents. The ultimate goal is to test whether volcano plots are evident in these systems and the LMWA reasoning (or the theory proposed by Ninham and collaborators) can be extended to nonaqueous solvents.

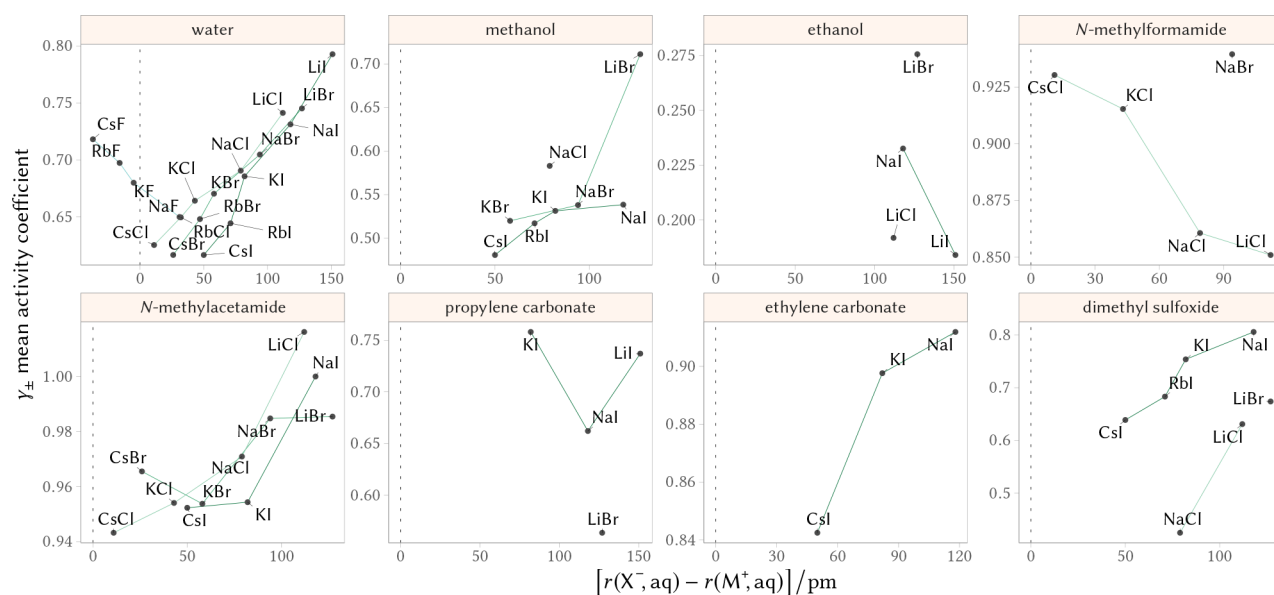


Figure 3. Inverted volcano plots of the activity coefficients. The electrolyte concentration is 0.4 mol kg⁻¹, except for methanol (0.07 mol kg⁻¹); propylene carbonate (0.18 mol kg⁻¹); ethylene carbonate and NMA, (0.09 mol kg⁻¹); DMSO and NMF (0.05 mol kg⁻¹). Colored lines are drawn to help identify the cation trends.

Solubility of Electrolytes. In order to ascertain if a volcano trend is exhibited in the solubility of electrolytes, the molal solubilities of alkali metal halides against the difference of their radii are plotted in Figures S51 and S52 of the Supporting Information.

A reversed volcano plot is observed in water, and, despite the scarce availability of information, it is retained in methanol and the homologous series of alcohols, although the solubility decreases rapidly along the series (the data are therefore plotted using a semilog scale). Also, there is a suggestion of an inverted volcano trend in the other protic nonaqueous solvents. In aprotic solvents, the left slope of the inverted volcano is missing. That is, where the fluorides series and chloride series are present, their solubility does not increase going toward smaller x -values. This is interesting and confirms what was observed previously with regard to the solvation of anions by aprotic solvents: it does not matter how much the ions are “mismatched”; the solvation of the fluoride and chloride anions in aprotic solvents is so unfavorable that the solubility of their salts is very low. This also demonstrates that the thermodynamics of the volcano plots at infinite dilution is not directly connected to the electrolyte solubility. This is also shown by the fact that, whereas the trend of KF–KCl–KBr dissolution energies observed in water is precisely the opposite of the trend in propylene carbonate,³⁶ the solubilities in the two solvents follow unrelated trends: KCl < KBr < KF < KI in water, and KF < KCl < KBr < KI in propylene carbonate.

Activity Coefficients. Activity coefficients are the ideal quantifier for ion–ion interactions in solution. For this analysis, we have also collected the activity and osmotic coefficients available in the literature for nonaqueous solvents. The data have been fitted (where no fitting was performed in the original paper) in order to interpolate to an intermediate concentration value so that as many electrolytes as possible can be compared. Plots of the activity coefficients versus concentration curves are shown in the Supporting Information, Figures S2–S4. Unfortunately, the data available for nonaqueous solvents are scarce.

The activity coefficients plotted versus the ionic radii difference are shown in Figure 3. It is important to clarify that the coefficients plotted for each solvent are for a specific salt concentration, which is not preserved across solvents due to different electrolyte solubility. In water we see the inverted volcano as proposed by Duignan (with Bromley’s B -coefficients) and mentioned by Fajans and Soniat et al.⁴² This same trend seems to show in methanol, NMA, DMSO, and EC (although just three points are available in this solvent). The trend in NMF is reversed. This is interesting because the same happens for the viscosity B -coefficient. The scarcity of data is problematic, but the trends observed in water seem to be respected. The lack of data does not allow any conclusions to be drawn regarding the differences between protic and aprotic solvents. It appears though, that the Law of Matching Solvent Affinity (LMSA), as proposed by Long et al.,⁴³ can be substantiated in these nonaqueous solvents, except for NMF.

The osmotic coefficients plot is provided in the Supporting Information, Figure S14, and the anion trends are highlighted in Figures S39 and S40. In addition, Figures S19 and S20 (lines showing anion trends) show the plots for electrolytes containing a polyatomic anion. Finally, Figures S29 and S30 (anion trends) and Figures S49 and S50 (cation trends) show the osmotic and activity coefficients of electrolytes with alkylammonium cations. For electrolytes containing polyatomic ions, the data are too scarce to allow for any consideration, but they are nonetheless shown in the Supporting Information for completeness.

GENERAL REMARKS

The work presented above is consistent with the following interpretation. Ions, or charged moieties in any solvent, form ion pairs that are in close contact when their size difference is most similar to the size difference of the cation and anion solvating groups of that solvent. The opposite is the case for ions of different sizes, that are poorly associated and retain their solvation shells. This is valid for anions and cations in

water and protic solvents, and for cations that share the same anion in aprotic solvents. This is not strictly valid when comparing anions that share a common cation in aprotic solvents. Putting this last category aside, where the particulars of the solvation of the anions are more strongly solvent specific and dominates, the formulation of a more general principle for the interaction of electrolytes in solvents that further develops the LMWA to encompass all solvents can be proposed. The specific-ion effects are dominated by, and largely originate from, the relative effective size of the anion and cation. The effective size is the size of the ion and the distance of the closest approach of the solvating group. The matching of effective ion size (MEIS) is therefore a useful and important general concept in understanding and predicting ion-specificity across solvents. That is, the principle of MEIS states that when the effective ion size of the cation and anion is matched, the ions lose part of their solvation shell to associate in solution, whereas when the effective ion size of the cation and anion is mismatched the ions do not associate. In addition to X-ray and neutron diffraction, an alternative and interesting way to estimate such effective sizes for electrolytes in solvents is made from the viscosity of solutions as proposed by Wynne.⁴⁴ The radius for the electrolyte would then have to be split into ionic radii. Wynne⁴⁴ also identifies the importance of the different nature of solvation of the anion and cation by the solvent. This association or otherwise explains a wide variety of ion-specific effects across a wide range of solvents. In relation to this prediction, our recent experimental findings¹³ on anion trends for size-exclusion chromatography and polymer brush conformation in water, methanol, formamide, dimethyl sulfoxide, and propylene carbonate show that the anion series vary between protic and aprotic solvents. Of course, additional data obtained using different solvents, electrolytes, and experiments need to be tested.

These observations demonstrate that, as already noted in our previous work,^{11,29} water is not a special solvent with respect to specific-ion effects, in that nonaqueous solvents exhibit similar phenomena.

Theoretical work is needed in order to understand the details of ion–solvent interactions and explain the qualitative trends presented here, and ultimately to develop a quantitative predictive theory of specific-ion effects that applies across multiple solvents.

CONCLUSIONS

The hypothesis that the law of matching water affinities arises from the ions themselves rather than their interaction with water or solvent is found to hold.

This analysis of volcano plots in nonaqueous systems has revealed a number of interesting features. The volcano plots are observed in nonaqueous protic and aprotic solvents, with the same trends as in water, with the exception of anion trends in aprotic solvents. It is shown that fundamentally the volcano trends arise from ion size. The volcano trends are manifest not only under standard conditions of infinite dilution but also at real concentrations.

As a consequence, it can be predicted that the ion trends observed in water will hold in protic nonaqueous solvents and that the cation trends observed in water will hold in aprotic nonaqueous solvents, whereas the anion trends might not be the same in water and aprotic nonaqueous solvents.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.8b00348.

Data sources and data treatment, and the complete set of volcano plots performed for alkali metal halides and salts containing polyatomic anions and cations in water and nonaqueous solvents (PDF)

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Notes

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