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A comparative investigation of mixing rules for property prediction in multicomponent electrolyte solutions

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Abstract A mathematical technique is developed to investigate physicochemical property prediction of solution mixtures from the corresponding properties of the pure dissolved systems, as is often expressed in empirical 'mixing rules' such as those of Young and of Zdanovskii. A systematic method to distinguish between the inherent characteristics of such rules is needed because experimental studies have proved indecisive. Sound mixing rules must be found to support current efforts in thermodynamic modelling where conventional approaches like the Pitzer equations lack robustness. Density differences relative to pure water, osmotic coefficients and heat capacities are investigated with mixtures including $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$ and $\{\text{NaCl} + \text{Na}_2\text{SO}_4\}(\text{aq})$ as specific examples representing common-anion and common-cation asymmetric strong electrolyte solutions respectively. Water activity curves for hydrochloric acid and the alkali metal chloride solutions are also considered. The results confirm that, at the present state of the art, differences between mixing rules are for the most part insignificant at 25 °C, being about the same or less than would be expected from experimental uncertainty. As the predicted differences are even smaller at higher temperature, it can be posited that all reasonably well-established mixing rules in the literature will give approximately equivalent and satisfactory predictions of solution properties under superambient conditions. This is particularly important, since the effects of temperature on the magnitude of ternary interactions are not well known from experiment.

Keywords Aqueous electrolyte · Mixing rules · Density · Water activity

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1 Introduction

Mixing rules { equations that describe the physicochemical properties of mixtures from the corresponding properties of the pure systems { are an essential tool in thermodynamic modelling given the practical importance of multicomponent electrolyte solutions, the infinite range of possible compositions and the general sparsity of relevant experimental data. In solution chemistry, the rules of Young [1], Zdanovskii [2] and Harned [3, p. 438] are best known but various others have also been described. Since such mixing rules typically originate empirically, their use in specific applications is often troubled by ambiguities. Without fundamental guidance it is not always easy to choose between them and in some cases (when the rule is linear) it is even unclear which concentration scale would be most appropriate. This paper describes a general mathematical technique capable of resolving such issues.

Considering the prohibitive cost associated with comprehensive experimental characterisation of multicomponent systems, it is unsurprising that methods of calculating the properties of multicomponent electrolyte solutions are seen as important. It follows that the advantages of mixing rules relative to the usual modelling functions for required physicochemical properties need to be assessed. Although the implementation of mixing rules can be more complicated, they tend inherently to be more robust, requiring fewer adjustable parameters. Added impetus comes from the serious limitations experienced with all current thermodynamic modelling frameworks [4].

In the context of mixtures, take for example the theoretical equations using ion-interaction parameters such as those of Pitzer [5] and of Scatchard (in the form of 'neutral electrolyte' [6] or 'ion-component' [7,8] equations), whose respective abilities to represent the properties of electrolyte solutions have been compared many times (see refs. [9-15]). In summary, the equations of the Scatchard theoretical framework contain a greater number of ternary interaction parameters and the agreement with measured data is better than Pitzer when more parameters are used [9, 13]. However, Pitzer's equations represent the experimental data more accurately when the same number of adjustable ternary parameters are employed [9-11]. Since the Pitzer equations also compare favourably with the other theoretical frameworks, they have become the method of choice for treating strong electrolyte solutions [16]. Only two adjustable parameters are in principle required to describe the interactions occurring in each common-ion ternary solution (i.e., in addition to those required for the binary systems). Unfortunately, ternary ion-interaction parameters can only be obtained from very reliable measurements [17] and data of sufficient quality to provide meaningful ternary interaction parameters are, in general, rare [17]. Consequently, approximate parameter values are often used, with one or both of the ternary coefficients often being set to zero [18, 19]. Even more complications arise if the modelling systems are treated inconsistently - ternary parameters must in particular be derived from an analysis using identical conditions to those under which the binary interaction parameters were determined and the same unsymmetrical mixing terms must be employed in their determination [11]. The appearance in the literature of different parameter sets thus makes it exceedingly difficult to achieve a unified and thermodynamically-consistent set of interaction parameters using the Pitzer theoretical framework for general thermodynamic modelling purposes [20].

As a practical alternative, methods based on empirical mixing rules have a long history, dating back at least as far as the early 20th century [21,22], i.e., around the same time as the development of the Debye-Hückel theory of electrolytes. Since then, considerable effort has gone into their development for various solution properties. This growing recognition of mixing rules has also prompted various comparisons: Pitzer equations have been compared to Zdanovskii's rule [2, 23,24] for calculations of water activities in mixed electrolyte solutions [25-31], and with Young's rule [1] for volumes [32] and heat capacities [33]. The appearance of different mixing rules has also naturally led to comparisons between them, usually in tests of their respective abilities to predict experimental data. The results have been varied: in some cases a particular mixing rule has been found to yield improved agreement with data [34-37]; yet in other cases, no conclusively better rule was found [38-45]. Investigating this kind of discrepancy motivates the present work. A systematic study of the inherent differences between mixing rules is described. Crucially, the magnitudes of the differences in the mixing rule predictions are compared to realistic assessments of the uncertainty in the corresponding experimental data.

2 Theory and Methods

2.1 Apparent molar volume and heat capacity

One of the clearest and most succinct descriptions of empirically-verified linear mixing is due to Young and Smith [1], who found that "the mean apparent molar volume of two electrolytes in an aqueous solution may be calculated from known values of the apparent molar volume of each electrolyte in the binary solution whose ionic strength is that of the ternary solution". This expression is outstanding for its conceptual simplicity. Mathematically, this rule, hereafter referred to as 'Young's rule for volumes', has the form

$$V_{\phi} = (m_1 V_{\phi,1} + m_2 V_{\phi,2}) / (m_1 + m_2) \quad (1)$$

where V_{ϕ} is the mean apparent molar volume of the ternary solution, m_1 and m_2 are the molal concentrations of the two electrolytes in the mixed solution, and $V_{\phi,1}$ and $V_{\phi,2}$ are the apparent molar volumes of the binary solutions (1 and 2) at the same ionic strength as the mixture.

Young's rule for volumes can be derived from the principle that the volumes of electrolyte solutions having equal molal ionic strength, when mixed, are additive.

Let the volume V of a ternary mixture be given by the sum of the volumes of its constituent binary solutions V_1 and V_2 , that is,

$$V = V_1 + V_2 \quad (2)$$

The volume of a binary solution of salt i containing w_i kg of solvent and having molality m_{0i} is

$$V_i = w_i (v_w + m_{0i} V_{\phi,i}) \quad (3)$$

where v_w is the volume of 1 kg of pure solvent at the same temperature and pressure as the solution. Using equation (3) in equation (2) gives

$$V = w_1 (v_w + m_{01} V_{\phi,1}) + w_2 (v_w + m_{02} V_{\phi,2}) \quad (4)$$

The total amount of solvent is $(w_1 + w_2)$ kg, so the molal concentrations of the salts in the ternary solution are

$$m_i = w_i m_{0i} / (w_1 + w_2), \quad i = 1, 2$$

Substituting this result into equation (4) and taking 1 kg as the total mass of solvent, the volume of the mixture is

$$V = v_w + m_1 V_{\phi,1} + m_2 V_{\phi,2} \quad (5)$$

The so-called 'mean' or 'experimental' apparent molar volume of a mixed electrolyte solution is [46]

$$V_{\phi} = (V - v_w) / \sum_i m_i$$

Substituting equation (5) into the above yields equation (1) [1,41]. For an arbitrary number of solutes the mean apparent molar volume of a mixture is given by

$$V_{\phi} = \left(\sum_i m_i V_{\phi,i} \right) / \sum_i m_i \quad (6)$$

This expression can also be cast in terms of the density of the solutions

$$\left(1000 + \sum_i m_i M_i \right) / \rho = \sum_j (1000 w_j + m_j M_j) / \rho_j$$

where ρ_j is the density of the j^{th} binary electrolyte solution at the same ionic strength as the ternary solution and M_j is the molar mass of solute j . This is equivalent to the mixing rule derived by Patwardhan and Kumar [35,47].

Following the same principles as in the derivation of Young's rule for volume, an analogous relation for the mean apparent molar heat capacity $C_{p,\phi}$ of mixed electrolyte solutions can be developed

$$C_{p,\phi} = \left(\sum_i m_i C_{p,\phi,i} \right) / \sum_i m_i \quad (7)$$

where $C_{p,\phi,i}$ is the apparent molar heat capacity of the binary solution of electrolyte i at the same ionic strength as the mixture. This is Young's rule for heat capacities [33]. Young's rule can also be generalised to other apparent molar quantities, for example, the apparent molar enthalpy, expansibility and compressibility (*e.g.*, [48{52} and references within).

2.2 Water activity

Numerous empirical mixing rules for the prediction of water activity in multicomponent electrolyte solutions have been proposed in the literature. In addition to Zdanovskii's rule (see [2,23,24,53,54]), there are additive mixing rules for vapour pressure lowering [55,3] and water activity [56], as well as multiplicative rules [35,57,58], and an explicit (that is, non-iterative) nonlinear equation approximating Zdanovskii's rule [59].

Table 1 Mixing rules in the literature for predicting water activity in multi-component solutions^a

Mixing rule	Representative equation	References
Zdanovskii	$\sum m_i/m_{0i} = 1$, at constant a_w	[2,53]
Additive ^{b,c,d}	$a_w = \sum y_i a_{w,i}$	[55,56]
Multiplicative ^{b,c,d}	$a_w = \prod a_{w,i}^{y_i}$	[57]
	$\ln a_w = \sum y_i \ln a_{w,i}$	[58,35]
Allahkverdov ^{c,e}	$\phi = \sum h_i \phi_i$	[60,61]
	$\phi = \sum h_i \phi_i / (1 + r)$, where	[59]
	$r = \sum_i \sum_{k>i} h_i h_k (1/\phi_i - 1/\phi_k)^2$	

^a a_w and ϕ are the water activity and osmotic coefficient of the mixture respectively; $a_{w,i}$ is the water activity in a binary solution having the same ionic strength as the mixture

^b The additive and multiplicative rules are each special cases [62] of the osmotic coefficient predictive equation [63]

^c y_i is the ionic-strength fraction of solute i in the mixture; h_i is the osmolality fraction of solute i in the mixture

^d Binary properties evaluated at the same ionic strength as the mixture

^e Binary solution osmotic coefficients evaluated at the same osmolality as the mixture

Each mixing rule is based on equations that define how the water activity of the mixture is calculated (Table 1). In the case of Zdanovskii's rule, the calculation is indirect: the linear mixing path with endpoint solutions having equal water activity is located iteratively [23]. The other mixing rules use direct methods, requiring the water activity of binary solutions at the same total concentration as the mixture, for example, the same ionic strength or osmolality.

Allahkverdov's mixing rule was developed most recently, so coverage of it in the literature is less extensive than that for the other rules. However, it is considered here, in spite of its nonlinear nature, because it approximates Zdanovskii's rule without requiring an iterative calculation [59].

The multiplicative and additive mixing rules share a common basis [62]. Consider the equation for the osmotic coefficient of a ternary mixture [60,61]

$$\begin{aligned} \phi &= (\nu_1 m_1 \phi_1 + \nu_2 m_2 \phi_2) / (\nu_1 m_1 + \nu_2 m_2) \\ &= h_1 \phi_1 + h_2 \phi_2 \end{aligned} \quad (8)$$

where $h_i = \nu_i m_i / (\nu_1 m_1 + \nu_2 m_2)$ is the *osmolality fraction* of solute i and ν_i is the number of moles of ions or molecules formed via dissolution of one mole of solute i . This equation is actually a simplification of Scatchard's neutral electrolyte expression [6], omitting ternary interaction parameters [41]. Substituting the relations $\ln a_w = -M_w (\nu_1 m_1 + \nu_2 m_2) \phi$ and $\ln a_{w,i} = -M_w \nu_i m_{0i} \phi_i$ ($i = 1, 2$) into equation (8) yields the relation [58,35]

$$\ln a_w = (m_1/m_{01}) \ln a_{w,1} + (m_2/m_{02}) \ln a_{w,2} \quad (9)$$

The other form of the multiplicative mixing rule [57] is obtained by exponentiating this result. The additive mixing rule for water activity [56] is obtained from equation (9) by making the approximation $\ln a_w \approx a_w - 1$. Thus, although it appears at first that there are many *different* mixing rules for predicting the water activity without ternary interaction parameters, most of them are substantially similar (Table 1).

2.3 Binary endpoint conditions

Inherently stated in each mixing rule are the concentrations at which the properties of the binary solutions are to be evaluated. For example, Young's rule evaluates binary solutions having equal ionic strength and Zdanovskii's rule evaluates binary solutions having equal water activity. In this work the different possibilities regarding which binary solutions to evaluate are called *binary endpoint conditions*.

The binary endpoint condition of constant ionic strength is often employed to predict the behaviour of mixed electrolyte solutions. However, the mathematical forms of Young's rule (equations (1) and (7)) and the multiplicative rule for water activity (equation (9)) do not change if different endpoint conditions are employed. In other words, equations (1), (7) and (9) can predict mixture properties based on evaluating binary solutions having equal molality, osmolality, solvent mass fraction, water activity, density or some other measure of concentration. In general, different endpoint conditions give different predictions of the mixture property. Comparing these different predictions is the key aim of this work.

Comparing the predictions of binary endpoint conditions using experimental data is problematic, since either real nonlinear mixing effects or systematic errors might favour erroneously one endpoint condition over another. An example is predicting the density, ρ , of $\{\text{NaCl} + \text{Na}_2\text{SO}_4\}$ (aq) mixtures using the binary endpoint conditions based on constant water activity, ρ_{zdan} , and constant ionic strength, ρ_{ionic} (Figure 1). The assumption of constant water activity gives better agreement with data at $I \approx 2.0 \text{ mol} \cdot \text{kg}^{-1}$, but the prediction based on constant ionic strength is better at $I = 1.5 \text{ mol} \cdot \text{kg}^{-1}$ and marginally better at $I \approx 3.0 \text{ mol} \cdot \text{kg}^{-1}$. Both predictions are good at $I = 1.0 \text{ mol} \cdot \text{kg}^{-1}$. Even with this simple ternary system it is impossible to decide conclusively from the experimental data which is the better endpoint condition. It turns out that particularly high precision is required to distinguish between the mixing rules. Any systematic error is evidently problematic. Since the primary intention here is to assess the inherent differences between predictions using different binary endpoint conditions, it is obviously necessary to avoid such experimental comparisons by using calculated, error-free data instead.

With any given quantity of solvent and solutes in a mixture, different partitions of the solvent among the pure solutes correspond to different binary endpoint conditions (Figure 2). Different endpoint conditions can then be compared by predicting the properties of ternary solutions using all possible solvent partitions (Figure 3). Binary electrolyte solution concentrations are calculated as $m_{01} = m_1/w_1$ and $m_{02} = m_2/(1 - w_1)$, where w_1 is the fraction of the solvent attributed to the first solute.

Pitzer equations can be employed reliably to describe the binary solutions, with parameters obtained from our JESS physicochemical property database [69] and optimisation methods described previously [67,68]. Being able to predict the properties of multicomponent electrolyte solutions at elevated temperatures is important since so few experimental data for mixed systems are available.



Fig. 1 Predictions of density at $t = 25\text{ }^{\circ}\text{C}$ in aqueous solutions of $\{\text{NaCl} + \text{Na}_2\text{SO}_4\}(\text{aq})$ using Young's rule (equation 1) and the endpoint conditions based on: **(a,c)** constant water activity; **(b,d)** constant ionic strength. I denotes ionic strength and y_1 is the ionic-strength fraction of NaCl in the mixture. Data taken from Millero and co-workers: [40] (Δ), [64] (\square), [65] (\circ) and [66] (\diamond).

3 Results

The mixtures $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$ and $\{\text{NaCl} + \text{Na}_2\text{SO}_4\}(\text{aq})$ are chosen as specific examples for investigation because they represent common-anion and common-cation asymmetric strong electrolyte solutions respectively. Several mixture concentrations (m_1, m_2) are adopted to reflect different composition ratios. Special consideration is given to the differences between constant ionic strength and constant water activity endpoint conditions due to recent interest in mixing rules based on constant water activity (for example, the works of Hu [70{73] and Wang [31,54,74])). The effects of increased temperature are investigated by comparing the predictions from Young's rule for volumes arising from different binary endpoint conditions at $100\text{ }^{\circ}\text{C}$. In all cases, the differences between the predicted endpoint conditions are contrasted with estimates of the experimental uncertainty. No comparisons are made between mixing rule predictions and actual experimental data; indeed it will be shown that definitive comparisons are generally beyond present experimental capability.

Certain issues limit the following comparison of mixing rules leading to an allowed set of conditions that we call 'feasible partitions'. While any partitioning of the solvent between the two solutes in a ternary mixture is mathematically possible, solubility places physical restrictions on the range that can sensibly be investigated. The concentration limits used in the optimisation of the Pitzer

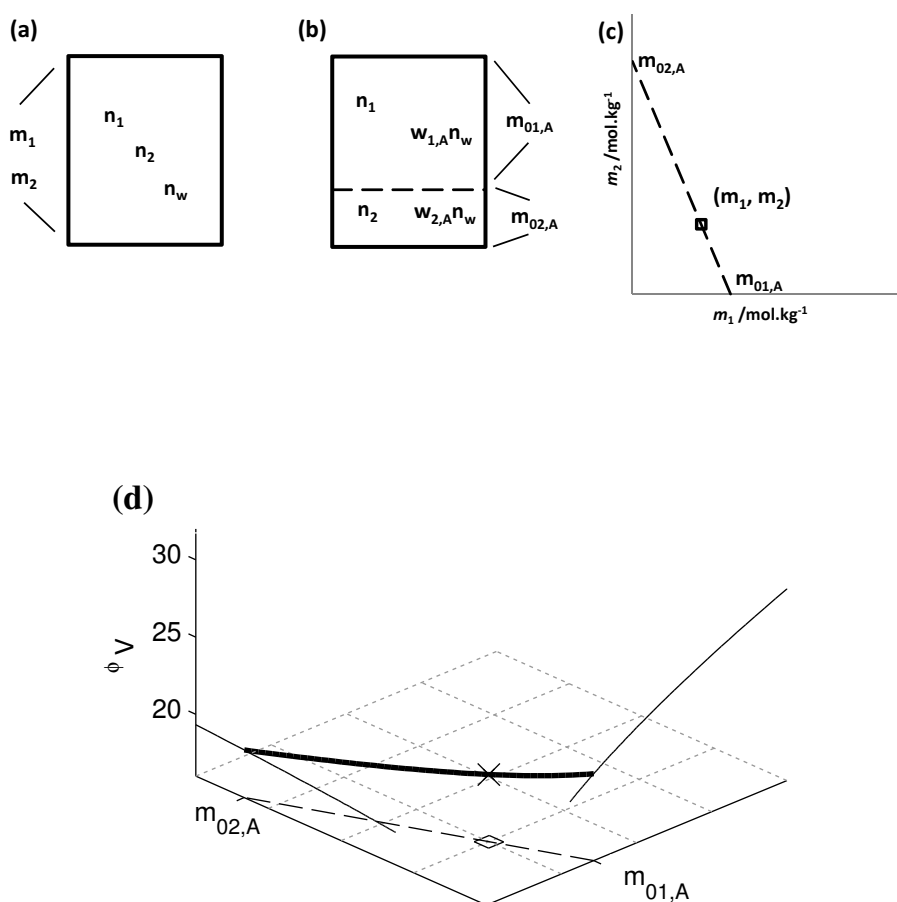


Fig. 2 Predicting the apparent molar volume of a ternary solution by partitioning the solvent arbitrarily among the pure solutes. **(a)** A ternary solution comprised of solutes 1 and 2 and water in amounts (n_1 , n_2 and n_w) mol. **(b)** The fraction of solvent notionally attributed to solute 1 is $w_{1,A}$. The remaining solvent is then attributed to solute 2. **(c)** This results in binary endpoint solutions having concentrations $m_{01,A}$ and $m_{02,A}$. **(d)** The apparent molar volume of the ternary solution (\times) is calculated from a linear combination of the apparent molar volumes at the endpoints, weighted by the respective mole fractions of the solutes in the mixture (equation (1)). The thin solid lines are the apparent molar volumes against concentration of the binary solutions. The thick solid line shows the predicted volumes for all mixture compositions along the mixing path (dashed line).

parameters describing the binary solution properties [67,68] further restrict the partition calculations

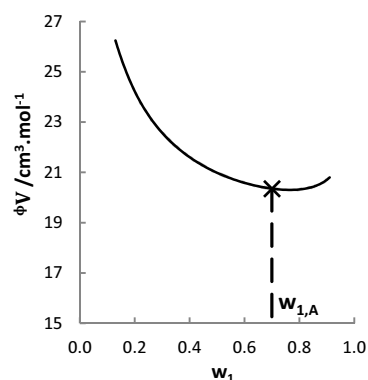


Fig. 3 The range of apparent molar volumes of a specific ternary solution calculated from Young's rule using different solvent partitions/mixing paths (solid curve). The particular solvent partition used in Figure 2 is indicated (\times).

3.1 Comparison of feasible solvent partitions

Density/volume

The calculated mixture densities relative to water at 25 °C are plotted in Figure 4. For each mixture of specified composition, the curve gives the various predictions using Young's rule for volumes based on all feasible binary endpoint conditions. The near constancy of the curves is remarkable. It is evident that even large changes in the concentrations of the endpoint electrolytes have little impact on the predicted mixture density. The densities corresponding to common values of w_1 which might be used in practice, such as equal ionic strength or water activity, are indicated in the Figure. It seems reasonable to expect that the w_1 values associated with other concentration variables (such as molarity and ionarity [41]) will not differ significantly from these positions.

The differences between the predictions based on different binary endpoint conditions are evidently quite small so it only remains necessary to establish whether they are experimentally distinguishable or not. In other words, do the predicted density values differ by more than the experimental uncertainty of density data? To answer this, Figure 5 shows the density values (from Figure 4) relative to the prediction based on Young's rule using the constant ionic strength endpoint condition.

The density values at 25 °C predicted using the common endpoint conditions differ by less than $0.001 \text{ g} \cdot \text{cm}^{-3}$ for $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$ and less than $0.004 \text{ g} \cdot \text{cm}^{-3}$ for $\{\text{Na}_2\text{SO}_4 + \text{NaCl}\}(\text{aq})$ (Figure 5). These density differences correspond to approximately 0.1% and 0.4% of the total solution density respectively. Near $T = 25 \text{ }^\circ\text{C}$, density measurements on ternary aqueous electrolyte solutions performed by independent investigators agree to within approximately 0.05% or better (*e.g.* [75]). This means that the various predictions would be difficult to separate using experimental data for the system $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$. However, it may just be possible to distinguish between some of the mixing rules for prediction at 25 °C based on highly accurate data for the system $\{\text{Na}_2\text{SO}_4 + \text{NaCl}\}(\text{aq})$.

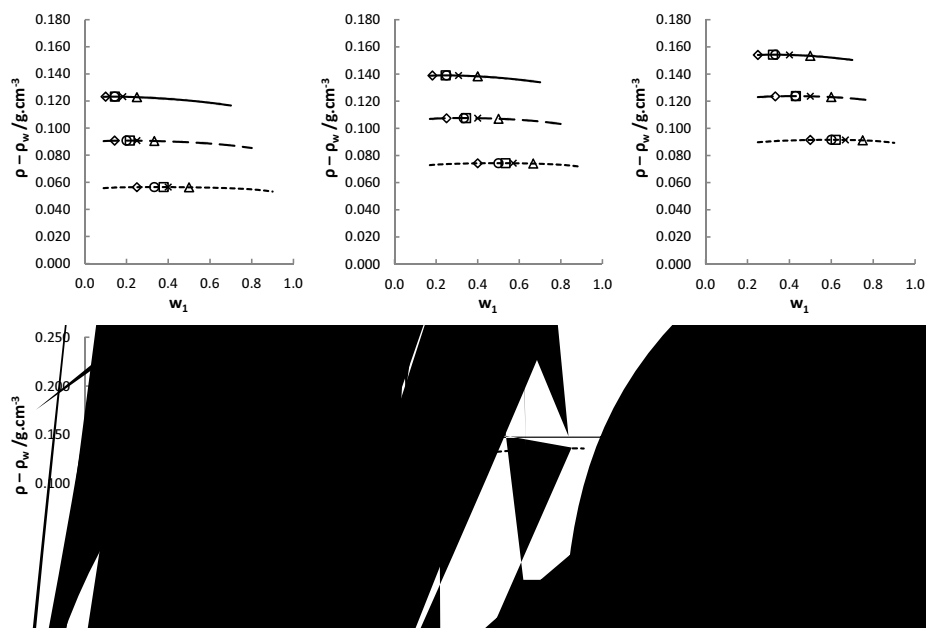


Fig. 4 Predicted values from Young's rule of the density difference relative to pure water against fraction of solvent assigned to the first solute at 25 °C. $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$ (top row); and, $\{\text{Na}_2\text{SO}_4 + \text{NaCl}\}(\text{aq})$ (bottom row). The concentrations are $m_1 / \text{mol} \cdot \text{kg}^{-1} = 0.5$ (left panels), 1.0 (middle), and 1.5 (right); and $m_2 / \text{mol} \cdot \text{kg}^{-1} = 0.5$ (dotted curves); 1.0 (dashed); and 1.5 (solid). Symbols correspond to various endpoint conditions: constant ionic strength (\diamond), molality (Δ), normality $\equiv \sum_c m_c z_c$ (\circ), osmolality (\times) and water activity (\square).

The calculated density differences between the feasible solvent partitions and the constant ionic strength endpoint condition at 100 °C are shown in Figure 6. The deviations are of similar magnitude to those at ambient temperature for $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$, but are smaller than the deviations at 25 °C for $\{\text{Na}_2\text{SO}_4 + \text{NaCl}\}(\text{aq})$ (*cf.* Figure 5). Since the experimental uncertainty of density data tends to increase with increasing temperature, a reasonable estimate of the accuracy achievable by independent investigators at 100 °C is 0.1% in the density. In this case, the different endpoint conditions would not be distinguishable for either of the representative ternary electrolyte systems considered here. By extension, at even higher temperatures the differences between the predicted density values will decrease below the experimental precision that can be achieved by an individual experimentalist, meaning that the matter of which endpoint condition to employ becomes irresolvable.

Water activity and osmotic coefficients

The predictions of the mixing rule for water activity (equation (9)) and Allakhverdov's rule (Table 1) are shown relative to the prediction based on constant ionic strength in Figure 7. The differences between the predicted osmotic coefficients are much more pronounced than those shown for density (Figure 5). In other words,

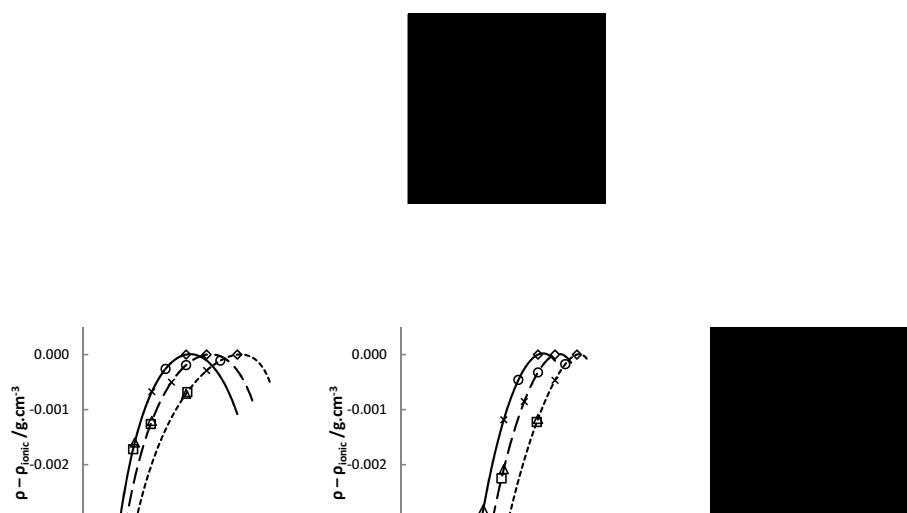


Fig. 5 Differences between the various density predictions and Young's rule using the constant ionic strength endpoint condition at 25 °C. $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$ (top row); and, $\{\text{Na}_2\text{SO}_4 + \text{NaCl}\}(\text{aq})$ (bottom row). The concentrations are $m_1 / \text{mol} \cdot \text{kg}^{-1} = 0.5$ (left panels), 1.0 (middle), and 1.5 (right); and $m_2 / \text{mol} \cdot \text{kg}^{-1} = 0.5$ (dotted curves); 1.0 (dashed); and 1.5 (solid). Symbols correspond to various endpoint conditions: constant ionic strength (\diamond), molality (Δ), normality $\equiv \sum_c m_c z_c$ (\circ), osmolality (\times) and water activity (\square).

it should be much easier to distinguish experimentally between these endpoint conditions (representing different mixing rules).

The typical difference between independent investigations of the osmotic coefficients of ternary electrolyte solutions is approximately 0.01 [24]. The range of osmotic coefficients that are achievable from feasible values of the solvent partition (curves in Figure 7) in solutions of $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$ and $\{\text{Na}_2\text{SO}_4 + \text{NaCl}\}(\text{aq})$ are larger than this.

Predictions based on the most common endpoint conditions differ by up to 0.2 in the osmotic coefficient of $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$. Since this system agrees well with Zdanovskii's rule [24], it appears that the endpoint conditions based on constant molality and constant osmolality do not adequately represent the real solution behaviour within experimental uncertainty. However, the predictions of the other endpoint conditions and Allahkverdov's rule differ by smaller amounts. It can be concluded that any one of these rules could be used to approximate the osmotic coefficients of this ternary system.

In solutions of $\{\text{Na}_2\text{SO}_4 + \text{NaCl}\}(\text{aq})$, the common binary endpoint conditions have inherent differences less than approximately 0.06 in their predictions of the osmotic coefficients. In particular the constant molality, constant osmolality and constant water activity (Zdanovskii's rule) endpoint conditions differ by less than or little more than the estimated uncertainty in osmotic coefficient data so their predictive capabilities are essentially equivalent. Allahkverdov's rule on the other

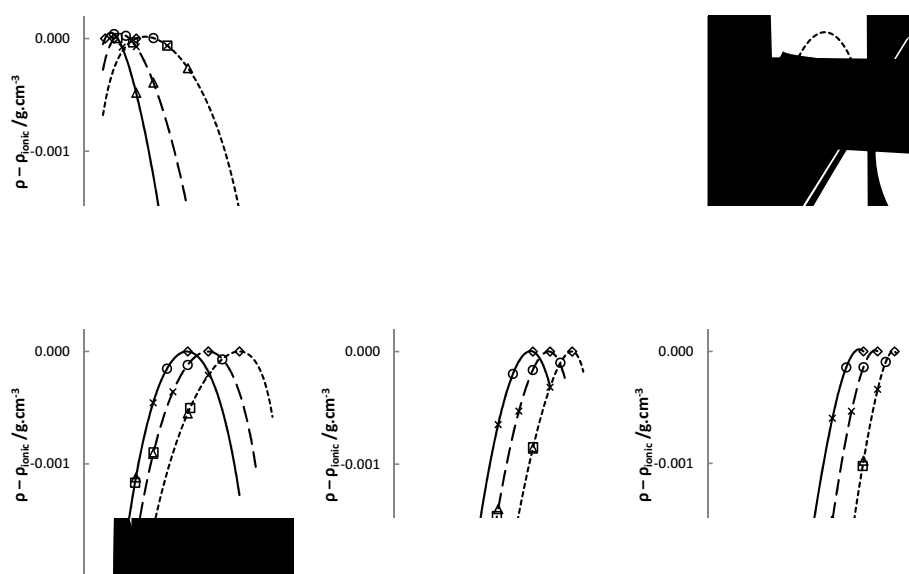


Fig. 6 Differences between the various density predictions and Young's rule using the constant ionic strength endpoint condition at 100 °C. $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$ (top row); and, $\{\text{Na}_2\text{SO}_4 + \text{NaCl}\}(\text{aq})$ (bottom row). The concentrations are $m_1 / \text{mol} \cdot \text{kg}^{-1} = 0.5$ (left panels), 1.0 (middle), and 1.5 (right); and $m_2 / \text{mol} \cdot \text{kg}^{-1} = 0.5$ (dotted curves); 1.0 (dashed); and 1.5 (solid). Symbols correspond to various endpoint conditions: constant ionic strength (\diamond), molality (Δ), normality $\equiv \sum_c m_c z_c$ (\circ), osmolality (\times) and water activity (\square).

hand shows large discrepancies from the other predictions; and the predictions based on constant ionic strength differ substantially from those based on constant water activity. It might therefore be possible to distinguish between the constant ionic strength endpoint condition and the other binary endpoint conditions using reasonably accurate data on this ternary system.

3.2 Comparison of the ionic strength and water activity mixing rules

Apparent molar volume

Water activity curves for hydrochloric acid and the alkali metal chloride solutions are shown in Figure 8. The dependences of water activity on solute molality are very similar for $\text{HCl}(\text{aq})$ and $\text{LiCl}(\text{aq})$. The $\text{KCl}(\text{aq})$, $\text{RbCl}(\text{aq})$ and $\text{CsCl}(\text{aq})$ curves are also in close agreement. The differences between the apparent molar volumes calculated using the constant ionic strength endpoint condition and the constant water activity endpoint condition are shown in Figure 9 as a function of molality for several ternary solutions of the alkali chlorides.

A reasonably optimistic estimate of the uncertainty associated with measurements of the apparent molar volume of moderately concentrated ternary electrolyte solutions is $\pm(0.1 \text{ to } 0.2) \text{ cm}^3 \cdot \text{mol}^{-1}$. It can be seen that in ternary systems where

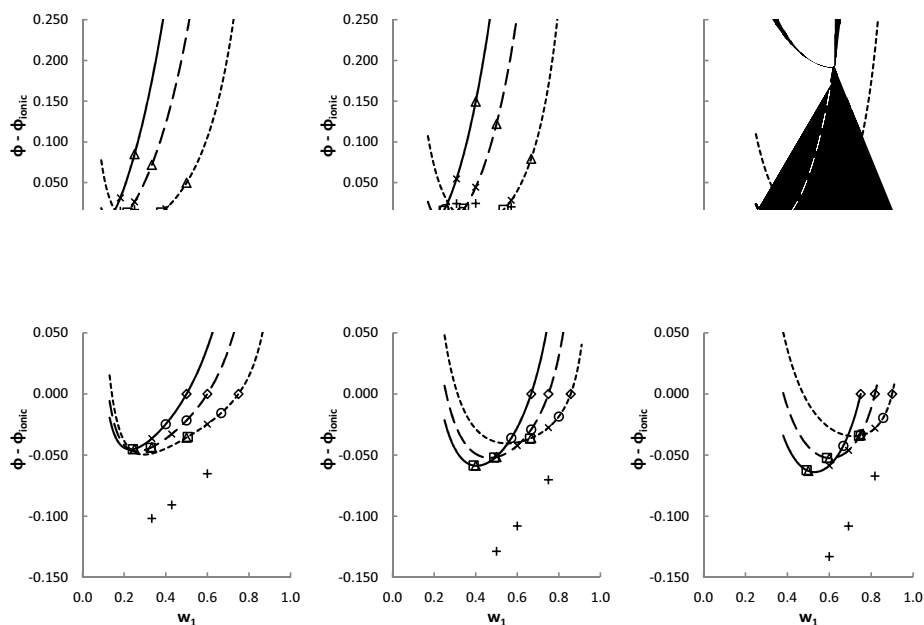


Fig. 7 Differences between the various osmotic coefficient predictions and the constant ionic strength endpoint condition at 25 °C. $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$ (top row); and, $\{\text{Na}_2\text{SO}_4 + \text{NaCl}\}(\text{aq})$ (bottom row). The concentrations are $m_1 / \text{mol} \cdot \text{kg}^{-1} = 0.5$ (left panels), 1.0 (middle), and 1.5 (right); and $m_2 / \text{mol} \cdot \text{kg}^{-1} = 0.5$ (dotted curves); 1.0 (dashed); and 1.5 (solid). Symbols correspond to various endpoint conditions: constant ionic strength (\diamond), molality (Δ), normality $\equiv \sum_c m_c z_c$ (\circ), osmolality (\times) and water activity (\square). Predictions based on Alahkverdov's rule [59] are also shown (+).

the constituent binary electrolytes have similar dependence of water activity with ionic strength, such as $\text{HCl} + \text{LiCl}(\text{aq})$ or $\text{KCl} + \text{RbCl}(\text{aq})$, the differences between the apparent molar volume predictions are well below this uncertainty estimate. In solutions where the pair of electrolytes have dissimilar water activity dependence with concentration the differences between the apparent molar volume predictions are less than $0.15 \text{ cm}^3 \cdot \text{mol}^{-1}$ in magnitude. Assessed realistically, this is not large enough to be distinguished experimentally.

Figure 10 shows the differences between the apparent molar volumes predicted based on constant ionic strength and constant water activity for several asymmetric ternary electrolyte solutions. The differences in $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$ and $\{\text{Na}_2\text{SO}_4 + \text{MgSO}_4\}(\text{aq})$ are found to be of the same magnitude as the typical experimental uncertainty. Hence, for these representative ternary electrolyte solutions, the constant ionic strength and the constant water activity endpoint conditions turn out to have equivalent ability to predict the apparent molar volume. However, the ternary solutions having a common cation, that is $\{\text{Na}_2\text{SO}_4 + \text{NaCl}\}(\text{aq})$ and $\{\text{MgSO}_4 + \text{MgCl}_2\}(\text{aq})$, show larger differences between the two predictions (approximately $1.0 \text{ cm}^3 \cdot \text{mol}^{-1}$ in magnitude). These differences should be sufficient for high-quality experimental measurements to favour one endpoint condition over the other (*i.e.*, be able to distinguish between different mixing rules).

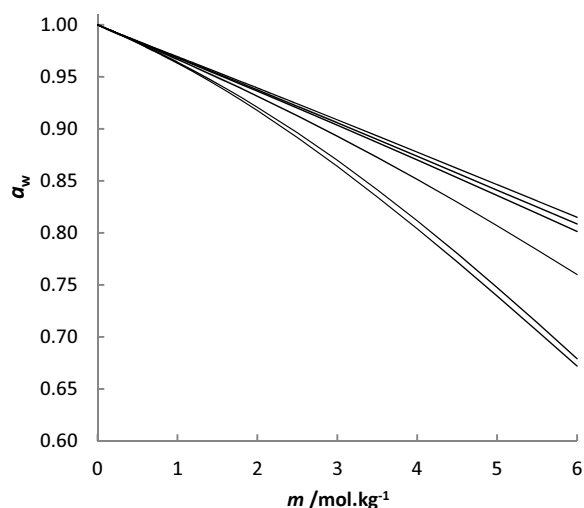


Fig. 8 Water activity against molality for hydrochloric acid and alkali metal chloride solutions at 25 °C. Values are calculated from the Pitzer equations [67,68]. Top to bottom: CsCl(aq), RbCl(aq), KCl(aq), NaCl(aq), LiCl(aq) and HCl(aq).

Apparent molar heat capacity

Differences between the predictions of the apparent molar heat capacity rule (equation (7)) using the ionic strength endpoint condition and the water activity endpoint condition appear in Figure 11.

A simple way to estimate the likely experimental uncertainty in the apparent molar heat capacity is to multiply the estimated uncertainty in the apparent molar volume by the ratio of the corresponding Debye-Hückel parameters for heat capacity and volume at 25 °C. Using $A_J/R = 3.8205 \text{ (kg} \cdot \text{mol}^{-1})^{1/2}$, $A_V = 1.8979 \text{ cm}^3 \text{ kg}^{1/2} \text{ mol}^{-3/2}$, and taking the uncertainty in the apparent molar volume as $\pm(0.1 \text{ to } 0.2) \text{ cm}^3 \cdot \text{mol}^{-1}$, the estimated uncertainty in the apparent molar heat capacity is thus estimated to be $\pm(1.7 \text{ to } 3.4) \text{ J} \cdot (\text{K} \cdot \text{mol})^{-1}$. This corresponds reasonably well with the $\pm 4 \text{ J} \cdot (\text{K} \cdot \text{mol})^{-1}$ estimate of Saluja *et al.* [76,33].

The differences between the predicted heat capacities for the systems $\{\text{NaNO}_3 + \text{NaCl}\}(\text{aq})$, $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$ and $\{\text{MgSO}_4 + \text{MgCl}_2\}(\text{aq})$ are of the same magnitude as the experimental uncertainty. In contrast, the ternary system $\{\text{MgSO}_4 + \text{Mg}(\text{NO}_3)_2\}(\text{aq})$ has differences significantly larger than the uncertainty estimate at high concentrations, meaning that apparent molar heat capacity measurements of concentrated mixtures could provide evidence favouring either the constant ionic strength or the constant water activity endpoint condition.

4 Discussion

The present results indicate that, at the present state of the art, predictions of the various mixing rules and binary endpoint conditions can be distinguished only with certain combinations of ternary electrolytes and physicochemical properties.

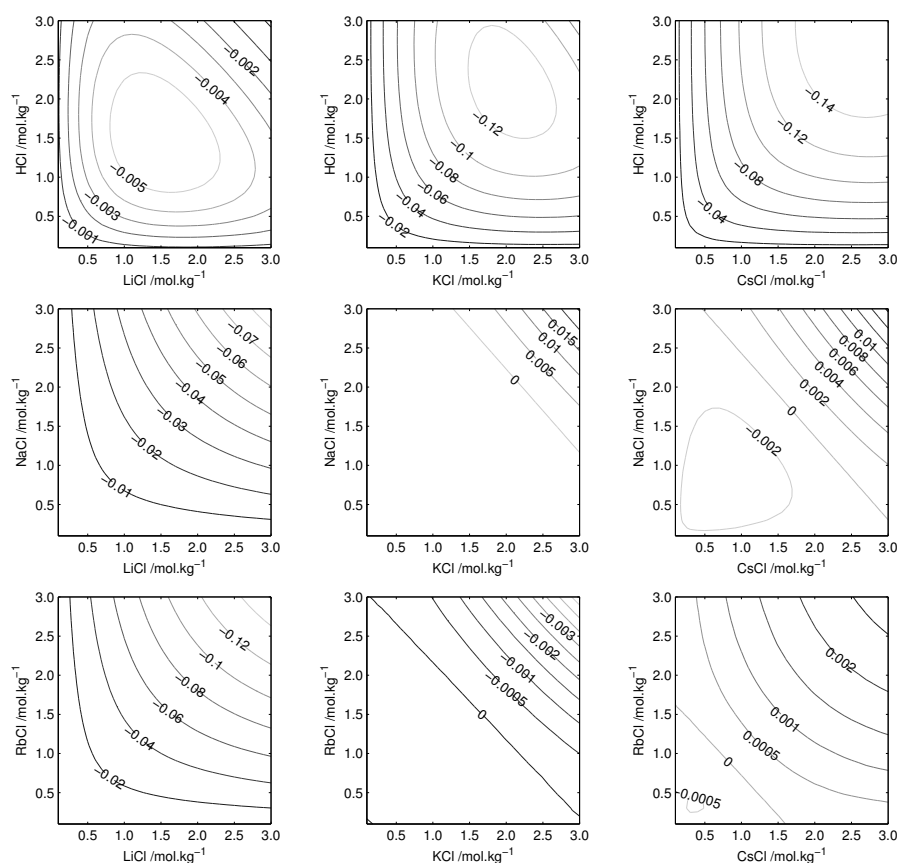


Fig. 9 Contour plots of apparent molar volumes in ternary alkali chloride solutions predicted by Young's rule using equal ionic strength endpoint conditions minus those using equal water activity at the endpoints. Units are $\text{cm}^3 \cdot \text{mol}^{-1}$.

If experimental results are available having the best precision that can be achieved by an individual investigator | for example, 0.003 in the osmotic coefficient under ambient conditions [77] | most of the predictions could, in principle, be compared usefully. However, in practice, the accuracy of mixing rules to predict ternary solution properties will be limited by the accuracy of representation of the binary sub-systems. Bear in mind that deviations of 0.01 to 0.02 between osmotic coefficients and values calculated with the Pitzer equations are common for concentrated binary electrolyte solutions [5, 68]. The contribution of these factors appears to be why comparisons with experimental data sometimes favour a particular mixing rule and sometimes do not. Investigators presenting empirical evidence regarding the superiority of one mixing rule or another need to be mindful of these difficulties.

The main outcome of this work is that since the differences between mixing rule predictions are often less than the experimental uncertainty, there is little empirical justification for choosing one binary endpoint condition (*i.e.*, one mixing rule) over another. However, because it is important to maintain thermodynamic

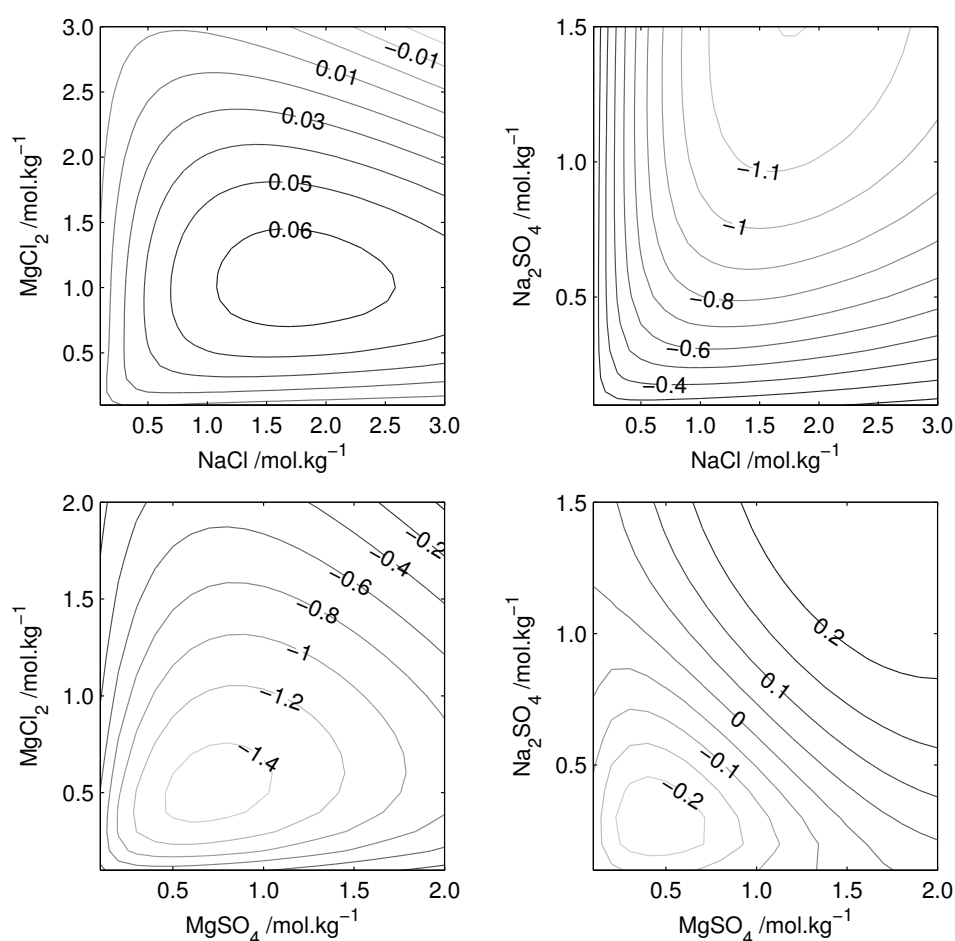


Fig. 10 Apparent molar volume difference contours (constant ionic strength predictions minus constant water activity predictions, $\text{cm}^3 \cdot \text{mol}^{-1}$) of $\{\text{NaCl} + \text{MgCl}_2\}(\text{aq})$, $\{\text{NaCl} + \text{Na}_2\text{SO}_4\}(\text{aq})$, $\{\text{MgSO}_4 + \text{MgCl}_2\}(\text{aq})$ and $\{\text{MgSO}_4 + \text{Na}_2\text{SO}_4\}(\text{aq})$.

consistency when calculating properties of multicomponent solutions, the same endpoint condition/mixing rule should be used to predict all of the relevant mixture properties. For this reason, the constant water activity endpoint condition is preferable to that based on constant ionic strength since the ionic strength is not defined for nonelectrolyte solutions.

It is also for this reason that specialised mixing rules, such as Allahkverdov's rule for osmotic coefficients [59], appear to hold little practical value, since they cannot be used to predict the thermodynamic behaviour of solutions comprehensively.

While there is some possibility binary endpoint conditions can be distinguished at 25°C , the present work suggests that the differences between predictions may well become too small to separate at higher temperatures. It can therefore be posited that all of the endpoint conditions/mixing rules established in the liter-

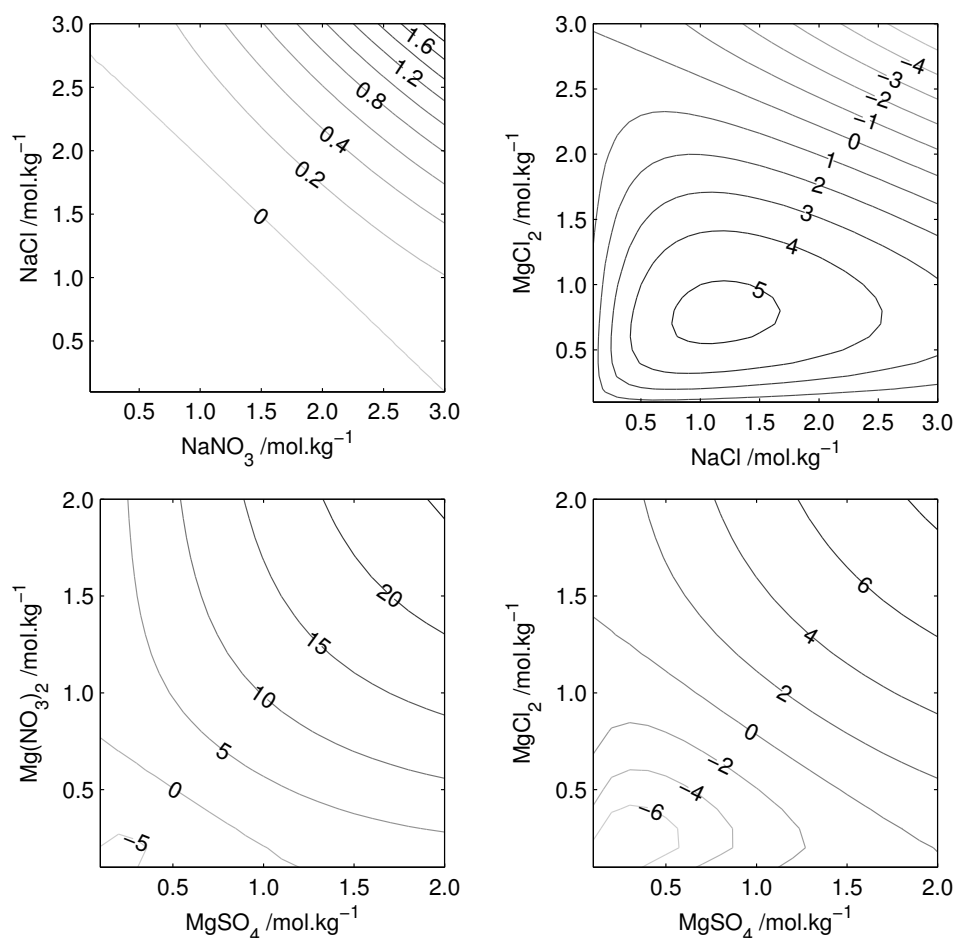


Fig. 11 Apparent molar heat capacity difference contours (constant ionic strength predictions minus constant water activity predictions, $J \cdot (K \cdot mol)^{-1}$) for $\{NaNO_3 + NaCl\}(aq)$, $\{NaCl + MgCl_2\}(aq)$, $\{MgSO_4 + Mg(NO_3)_2\}(aq)$ and $\{MgSO_4 + MgCl_2\}(aq)$.

ature will give approximately equivalent and reasonable predictions of solution properties under superambient conditions. This is important, since the effects of temperature on the magnitude of ternary interactions are not well known from experiment.

5 Conclusion

A novel method is here proposed that generalises predictions from well-known mixing rules. This indicates that predicted bulk property values are surprisingly insensitive to large changes in the way the solvent is partitioned among the pure solutes in a multicomponent mixture. In particular, comparison of the differences between the predicted values and the typical experimental uncertainty demonstrates that

the property predictions for a variety of ternary solutions are essentially equivalent. It follows that apparent agreement with experiment is an insufficient basis for selecting one binary endpoint condition over another. A conclusion to this effect has been drawn previously [16].

Mixing rules have a useful role in the prediction of physicochemical properties of multicomponent electrolyte solutions. Especially for bulk solution properties, mixing rules yield good approximations for all but the most nonideal interacting systems. The properties of minor components (for example trace activity coefficients and partial molar volumes) are more difficult to reproduce [3, 62]. However, this is because of general numerical sensitivities rather than the mathematical form of the mixing rules.

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