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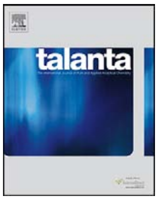

JESS, a Joint Expert Speciation System—V: Approaching thermodynamic property prediction for multicomponent concentrated aqueous electrolyte solutions[☆]

Darren Rowland*, Peter M. May

School of Chemical and Mathematical Sciences, Murdoch University, Murdoch WA 6150, Australia

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ABSTRACT

Considerable difficulties persist in modelling the thermodynamics of multicomponent aqueous electrolyte solutions, especially at high concentrations. The widely adopted Pitzer formalism suffers from severe disadvantages, particularly with the combinatorial increase in mixing parameters required in multicomponent systems. As an alternative, the simple mixing rules of Young, of Harned and of Zdanovskii have been employed to predict the properties of mixtures using only the properties of the binary constituents with few or no additional parameters. Among these, Zdanovskii's rule is particularly promising because it constitutes a fundamental criterion for ideal mixing, i.e. when solutions having the same solvent activity are mixed in any proportion, the solvent activity remains unchanged. Many mixtures of strong electrolyte solutions are known from experiment to obey Zdanovskii's rule. This is important because application to aqueous electrolyte systems of practical interest has been hindered due to the process-intensive determination of water activities using the Gibbs–Duhem relation. This paper describes an alternative method which efficiently calculates the water activity of a multicomponent solution obeying Zdanovskii's rule. Some specific examples of the method are presented and various applications considered. In some systems, where deviations from Zdanovskii's rule occur, a single empirical parameter can be obtained and can be easily incorporated into the calculations.

1. Introduction

Considerable difficulties persist in modelling the thermodynamics of multicomponent aqueous electrolyte solutions, especially at high solute concentrations. This imposes restrictions on the applications of such models, which are needed in a wide variety of practical contexts such as in measurement science, oceanography, biochemistry and hydrometallurgy [2].

Although the Pitzer formalism [3] is frequently adopted in the chemical literature it suffers from severe disadvantages. Especially when temperature and pressure changes are involved, the equations require many empirical parameters and are susceptible to correlation. They therefore tend to be ill-conditioned, and parameter fitting becomes highly dependent on the range of available data [4]. Their predictions are thus subject to serious error propagation.

These issues become profoundly problematic with multicomponent systems because of the combinatorial increase in the number of Pitzer parameters needed and because of the relatively few experimental studies made on mixed electrolyte solutions. Reactions between the chemical species in solution, which often dominate in applied systems, add significant further complication.

It has been evident for some time that a different, more fundamental, theoretical approach to modelling aquatic chemistry is needed to control the number of modelling parameters and to cope better with extrapolations into multicomponent spaces that have not been experimentally characterised. A useful concept has been to describe the properties of binary systems (i.e. aqueous solutions with only one electrolyte) empirically but to employ simple linear mixing rules to predict the properties of their mixtures [5,6]. Good examples of such rules are those of Young, of Harned and of Zdanovskii [2].

Zdanovskii's rule [7–9] in particular is promising. Zdanovskii's rule states that when solutions having the same thermodynamic activity of water are mixed in any proportion the solvent activity remains unchanged. This constitutes a fundamental criterion for ideal mixing, i.e. an effective lack of interaction between component electrolytes when there is no change in solvation [2]. Many strong electrolyte solutions are known from experiment to obey Zdanovskii's rule [10–12] so their mixtures can be accurately described with no additional parameters. Moreover, in other less ideal systems (as described below), it is often the case that the observed deviations are small and can be well represented at constant temperature by only a single additional empirical parameter. This is a major advantage over Pitzer equations which, even at

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[☆] Part IV is reference [1].

* Corresponding author. Tel.: +61 8 9360 2916.
E-mail address: D.Rowland@murdoch.edu.au (D. Rowland).

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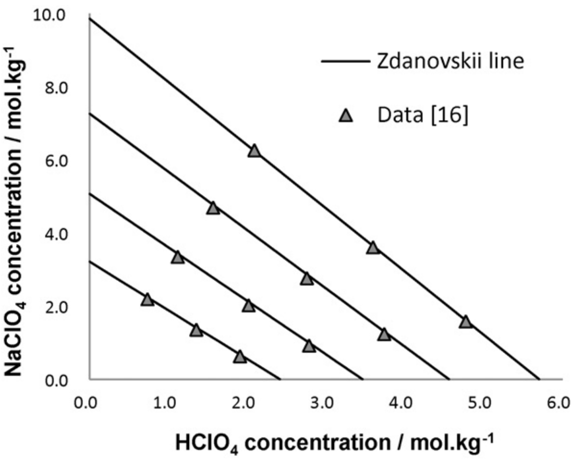

Fig. 1. Zdanovskii isopiestic plot.

constant temperature, invoke two extra parameters for each electrolyte combination.

Unfortunately, to exploit Zdanovskii's rule in a conventional manner requires the water activity of the mixture to be determined iteratively by integrating the Gibbs–Duhem relation [13, p. 33]. Even nowadays, this is such a process-intensive calculation that it prohibits general modelling applications involving aqueous electrolyte systems of industrial, environmental or biological interest.

Several workers including Wang (e.g. [14] and references therein) and Clegg and Seinfeld (e.g. [15] and references therein) have shown the effectiveness of Zdanovskii's rule (and extensions upon it) as it pertains to predicting the thermodynamic properties of mixtures such as aqueous electrolytes and non-electrolytes, aerosols and molten salts. However it has not been made sufficiently clear – for example in an algorithm – how the estimation of properties in the ternary or higher systems follows from the knowledge of the binary properties. The true test of the applicability of Zdanovskii's rule (or other mixing rules) is not only the accuracy of predictions but also the computational cost associated with those predictions. This burden must be brought in line with the comparative cost of non-iterative schemes if it is to be used in large-scale environmental and industrial process applications. Accordingly, in this work we present the equations used in our algorithm and discuss some methods to improve its performance.

2. Theory and equations

2.1. Zdanovskii's rule

The specific goal of this work is to determine the water activity of a multicomponent aqueous solution given its composition, e.g. given the concentrations of A and B in the ternary mixture A–B–H_2O, find the water activity, a_w. This can be accomplished by assuming the Zdanovskii relationship, i.e. mixing occurs ideally along a path of constant water activity. An example of a ternary system featuring strong agreement with Zdanovskii's rule is shown in Fig. 1. Each of the dashed lines connects binary solutions having equal water activity. The data lie almost exactly on the corresponding iso-activity line. In general, the key then is to find the concentrations of all binary component solutions which have the same water activity as the mixture.

In the simplest case of a ternary mixture, Zdanovskii's rule can be expressed as

$$1 = \frac{m_1}{m_{10}} + \frac{m_2}{m_{20}}$$

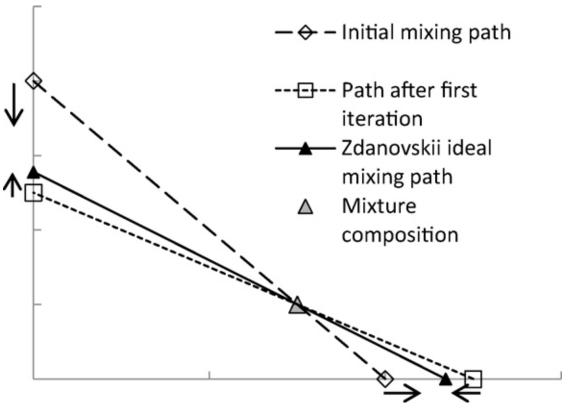

Fig. 2. Illustration of the convergence of the current algorithm.

Here m_i is the concentration of solute i in the mixture and m_{i0} is the concentration of a binary solution of solute i with water activity equal to that of the ternary mixture. More generally for a mixture of n solutes, the ideal mixing condition satisfies

$$1 = \sum_{i=1}^{n} \frac{m_i}{m_{i0}}$$

The iterative algorithm outlined in Appendix A utilises the fact that every other (non-Zdanovskii) mixing path involves a change in water activity, with a sign that systematically indicates how to adjust concentration estimates for the binary solutions 'being mixed'. Fig. 2 illustrates how the algorithm progresses. The initial concentration estimate results in binary solutions with unequal water activity (square markers). However, the direction for adjustment – indicated by arrows – is known because the a_w function is monotonic decreasing with increasing concentration. The algorithm iterates over mixing paths until the Zdanovskii mixing path of constant water activity is found. The determination of the water activity throughout this paper occurs to within a tolerance of 10^{-5}.

3. Implementation

The method has now been fully implemented as part of our JESS (Joint Expert Speciation System) software package [1,17] [http://jess.murdoch.edu.au]. It has proved to be a general and very fast method for predicting the thermodynamic properties of aqueous solutions containing mixed strong electrolytes in high concentration.

The derivative of water activity for each solute is required in order to construct the Jacobian matrix for Newton–Raphson updates. A number of different schemes were trialled in an investigation of the optimal settings for minimising the number of function evaluations required to achieve convergence. Table 1 summarises the results for an example system of 4 electrolytes. Both analytical and numerical derivatives were trialled. Where numerical derivatives were used, the first determination of the Jacobian used analytical derivatives. 'J' is the number of iterations for which the Jacobian matrix was evaluated. 'Iter.' is the number of times the matrix equation was solved. 'F' is the total number of times the

Table 1
Convergence results for a system of 4 electrolytes.

Derivative method	J	Iter.	F	$10^6\chi$
Analytical	3	4	28	1.0
Analytical	1	13	56	6.0
Analytical	2	5	28	5.0
Numerical	4	5	24	1.9

water activity or its derivative was calculated. χ gives the level of convergence achieved, representing the range over water activity values.

When the Jacobian is calculated every iteration, analytical derivatives are more accurate than numerical but the cost of computation (measured in function evaluations) is greater. The results indicate that although the correct solution is obtained using constant Jacobian approximation, the quality of the solution deteriorates and the number of iterations increases. The best balance between speed and accuracy occurs where numerical derivatives are used.

The excess Gibbs energy can be calculated when the activity of the solvent and each of the constituent electrolytes is known. The activity coefficient γ_i of an electrolyte in a mixture is related to its isopiestic concentration via the relation

$$\gamma_i = \frac{\nu_i m_{i0} \gamma_{i0}}{\sum \nu_j m_j}$$

where ν_i is the number ions in the formula for electrolyte i and γ_{i0} is the activity coefficient in the binary solution (obtained using the Pitzer equations) and the summation is over all electrolytes in solution ([12] and references within).

4. Predictions

Some mixed electrolyte systems, for which the water activities have been well characterised experimentally, were used in order to test the predictive performance of the algorithm. (This effectively limited this part of the study to comparisons with simple ternary systems.)

Table 2 compares literature data with predictions made using the present algorithm for various electrolyte systems. The concentration of each component is given in mol kg^{-1}, where m_1 refers to the first named component and m_2 refers to the second component. The experimental value of water activity is denoted a_w (meas.). In cases where either the osmotic coefficient or isopiestic

Table 2
Comparison of experimental and simulated data.

	m_1	m_2	a_w (meas.)	a_w (calc.)	% a_w (dev.)
KCl + KBr [18]	0.8116	1.2338	0.9342	0.9342	0.001
	1.6383	0.4178	0.9342	0.9343	0.009
	0.4244	1.6141	0.9342	0.9343	0.004
	1.2242	0.8247	0.9342	0.9343	0.012
	1.8508	1.1813	0.9019	0.9019	0.003
	1.2566	1.7663	0.9019	0.9019	0.006
	0.6225	2.3921	0.9019	0.9018	0.016
	2.4638	0.5783	0.9019	0.9019	0.000
	1.9242	2.4018	0.8581	0.8576	0.058
	2.7351	1.5988	0.8581	0.8578	0.033
	0.9999	3.3175	0.8581	0.8573	0.086
	3.5560	0.7895	0.8581	0.8579	0.022
$NH_4Cl + BaCl_2$ [12]	0.8305	0.5517	0.9462	0.9461	0.008
	1.2179	0.3041	0.9462	0.9462	0.002
	0.2322	0.9329	0.9462	0.9461	0.011
	0.5050	0.7592	0.9462	0.9461	0.009
	0.3020	1.2015	0.9279	0.9279	0.002
	1.6145	0.4009	0.9279	0.9279	0.001
	1.0875	0.7234	0.9279	0.9278	0.007
	0.6599	0.9845	0.9279	0.9278	0.007
	1.2717	0.8497	0.9144	0.9141	0.030
	1.8950	0.4783	0.9144	0.9142	0.021
	0.3454	1.3976	0.9144	0.9143	0.016
	0.7632	1.1509	0.9144	0.9141	0.030
$Na_2SO_4 + MgSO_4$ [19]	0.400	0.400	0.9781	0.9779	0.02
	0.500	0.500	0.9729	0.9725	0.04
	0.600	0.600	0.9675	0.9669	0.06
	0.700	0.700	0.9620	0.9612	0.08
	0.800	0.800	0.9562	0.9551	0.11
	0.900	0.900	0.9500	0.9487	0.14
	1.000	1.000	0.9435	0.9420	0.16
	1.200	1.200	0.9289	0.9271	0.19
	1.400	1.400	0.9121	0.9103	0.20
	1.600	1.600	0.8928	0.8912	0.18
	1.800	1.800	0.8706	0.8697	0.10
	2.000	2.000	0.8455	0.8458	0.03
$CaCl_2 + MgCl_2$ [20]	1.5492	0.3805	0.8710	0.8660	0.57
	1.7814	0.3044	0.8650	0.8510	1.62
	2.4999	0.2812	0.7705	0.7748	0.55
	1.9557	0.8145	0.7634	0.7714	1.04
	2.2632	0.5684	0.7633	0.7662	0.38
	1.6398	1.0730	0.7633	0.7759	1.64
	1.8517	1.8600	0.6645	0.6423	3.34
	1.4470	2.1714	0.6643	0.6511	1.99
	3.7015	0.4008	0.6035	0.6070	0.57
	2.3332	2.5136	0.5167	0.4854	6.05
	1.4557	3.3767	0.5028	0.4774	5.05
	1.9773	2.9655	0.5028	0.4679	6.94

Table 3
Survey of common-ion ternary aqueous systems.

System	Ref	# data	Mixing parameter (b)	% a_w deviation		
				A	B	C
NaCl + KCl	[24,18]	89	−0.01	0.12	0.11	0.012
$HClO_4$ + $LiClO_4$	[16]	15	0.0035	0.043		0.013
$HClO_4$ + $NaClO_4$	[16]	64	−0.0073	0.37	0.57	0.32
$LiClO_4$ + $NaClO_4$	[16]	33	0.013	0.11	0.29	0.017
NaCl + NaBr	[18]	8	0.0004	0.0049		0.0046
LiCl + $NiCl_2$	[25]	8	0.012	0.0036		0.0015
Na_2SO_4 + $MgSO_4$	[19]	16	−0.0063	0.067	0.054	0.065
KCl + $MgCl_2$	[26]	34	−0.036	0.38	0.26	0.082
K_2SO_4 + $MgSO_4$	[27]	22	0.049	0.15		0.15
NH_4Cl + $BaCl_2$	[12]	12	−0.004	0.01		0.0051
NaCl + $NaNO_3$	[28]	13	−0.0089	0.08	0.15	0.044
NaBr + KBr	[18]	12	−0.014	0.077		0.018
KCl + KBr	[18]	12	−0.002	0.019		0.013
KCl + KNO_3	[28]	8	0.00013	0.011		0.011
$CaCl_2$ + $MgCl_2$	[20]	43	−0.032	0.73		0.5
$MgCl_2$ + $MgSO_4$	[29]	44	0.041	0.05	1.84	0.027
$MgCl_2$ + $Mg(NO_3)_2$	[30]	23	0.0045	0.12	0.26	0.048
$HClO_4$ + $UO_2(ClO_4)$	[31]	60	−0.013	0.31	0.33	0.22
$NaClO_4$ + $UO_2(ClO_4)$	[31]	60	−0.0049	0.26	0.47	0.26
$Ca(NO_3)_2$ + $Mg(NO_3)_2$	[30]	15	−0.016	0.34	0.69	0.10
$CaCl_2$ + $Ca(NO_3)_2$	[30]	17	−0.0088	0.65		0.45

(A) Zdanovskii deviation without mixing parameter.
(B) Zdanovskii deviation reported in [9].
(C) Zdanovskii deviation using mixing parameter.

ratio was reported the values have been converted to water activity for convenience of comparison. The predicted values of water activity are reported as a_w (calc.) and the absolute values of percentage deviation between the measured and calculated values as $\%a_w$ (dev.).

The systems here were chosen to reflect the various types of strong electrolytes which can be treated with this method. The parameters chosen to model the binary electrolytes were those of [3]. Each of the systems can be seen to exhibit very good agreement with the linear mixing rule. Almost all systems shown obey Zdanovskii's rule to within the error of experiment. The largest deviations occur for the system $CaCl_2$ + $MgCl_2$ but even in this case the experimental values obey Zdanovskii's rule reasonably well for $a_w > 0.76$.

5. Adjustments for nonideal behaviour

When solutions of equal water activity are mixed to become multicomponent systems the water activity may vary to some extent, i.e. not behave in full accordance with Zdanovskii's rule. This type of nonideal mixing presents complications on many levels. Some kind of mixing parameter must be introduced to describe the system accurately and optimising such parameters necessitates experimental characterisation of the multicomponent system.

The ternary solution may then satisfy a mixing rule which incorporates a deviation from ideality, for instance

$$1 = \frac{m_1}{m_{10}} + \frac{m_2}{m_{20}} + \Delta \qquad (1)$$

The way this function can be implemented in conjunction with the primary algorithm is detailed in Appendix B.

6. Results

6.1. Comparison of calculated and observed results

When experimental data for the osmotic coefficient or water activity are available it is possible to optimise the data and obtain a parameter which reflects the extent of deviation from Zdanovskii linearity and which can be used to make improved predictions. To illustrate this effect we have chosen a simple one-parameter model for describing nonideal mixing, that is $\Delta = b(m_1 m_2/m_1 + m_2)$ in Eq. (1). This model was first proposed in [23] to describe the deviation from ideal mixing in a number of ternary solutions. It is adequate for our purposes given that the number of data points in most available data sets is quite limited.

Table 3 contains the analysis of 21 ternary electrolyte systems, all containing a common ion and measured at 25 °C and 1 bar. References to the original sources are given, as well as the number of data points used in the analysis. In most cases all of the data from the given references have been used. In the least-squares optimisation, all data have been given equal weight up to ionic strength 4.0 mol kg^{-1} after which the weights have been scaled as 4.0 mol kg^{-1}/[ionic strength]. Agreement between measured and calculated values is expressed as the average percent deviation for the data set (A).

This analysis is similar to the treatment in [10]. Where available, the values for average deviation calculated in that paper are shown (B). The agreement between columns (A) and (B) is reasonable. Small differences arise because the data sets differ, as does the method of water activity determination in the binary solutions (Chen et al. [10] used an nth degree polynomial ($n \sim <10$) fit to the data. This paper uses Pitzer models for osmotic coefficient as described above). The percent average deviation including the mixing parameter (C) makes clear that most of the systems are more

Table 4
New optimised Pitzer parameters for some 2:1 electrolytes.

Electrolyte	References	# data	Max m	β^0	β^1	C^ϕ
$Ca(NO_3)_2$	[13,21]	62	6.0	0.1673	1.662	−0.00675
$Mg(NO_3)_2$	[13,22,21]	108	5.02	0.3309	1.719	−0.00662

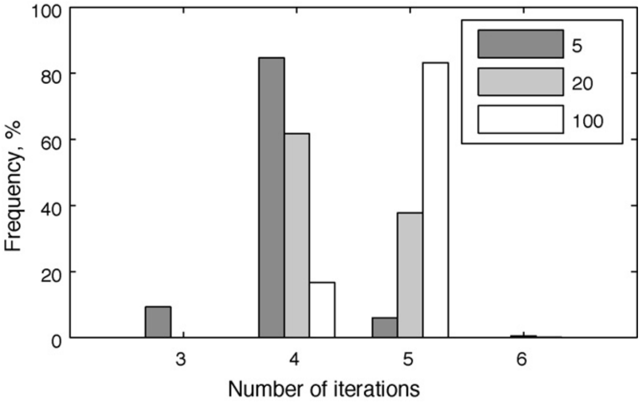

Fig. 3. Convergence behaviour for large multicomponent systems.

accurately represented by including the parameter. It is important to note, however, that substantive deviations from ideal mixing (Zdanovskii's rule) are rare.

6.2. Use of Pitzer parameters

It is well known that using Pitzer models beyond the concentration range of parameter optimisation can lead to large inaccuracies. This is particularly evident for electrolytes of the 2:1 type investigated in this study. Evidently, the binary solutions must be accurately described for the water activity in the mixture to be determined accurately. Rather than limit the approach only to those ternary solutions whose concentration is sufficiently low to be adequately modelled using published parameters, we have optimised new sets of binary data Pitzer parameters (β^0, β^1, C^ϕ) applicable to higher concentrations [1].

Presented in Table 4 are the results determined using activity and osmotic coefficients for the binary electrolytes shown. The upper limit of concentration used in the parameter optimisation for the parameters is also shown. For all other binary salts the parameters in [3] were used.

6.3. Algorithm performance with large multicomponent mixtures

Computational efficiency is of high importance when considering the applicability of Zdanovskii's rule (or other mixing rule approaches) to large multicomponent mixtures, such as those encountered in industrial processes and environmental studies.

Fig. 3 presents the number of iterations required for convergence for large multicomponent mixtures. Systems comprising 5, 20 and 100 electrolytes were simulated 1000 times each with random mixture compositions. The number of iterations required for convergence increases only marginally as the system size grows, showing that the present algorithm is well suited to evaluating the thermodynamic properties of large mixtures.

7. Discussion

It has long been understood that the solvent is a fundamental driver of solution thermodynamics and, in particular, of the activity coefficients of solutes. For this reason, Robinson and Stokes [13, p. 248] developed their well known ionic hydration models more than half a century ago. Initially, these models proved very successful in rationalising the activity coefficients of many strong electrolytes in aqueous solution but they have, evidently, not since fulfilled their early promise, especially in the case of mixed solutions. It is clear nowadays from dielectric relaxation spectrometry [32,33] and other techniques that hydration processes are too dynamic and subtle to be well characterised by functions based on simple hydration numbers. On the other hand, a description of how water activities behave in multicomponent mixed electrolyte solutions can be achieved using the present algorithm without resort to activity coefficients other than those of the binary solutions. This therefore presents an opportunity to develop better activity coefficient models for chemical species than have been available hitherto. We envisage that this will confer significant advantage in chemical speciation modelling by further reducing the number and the uncertainty of parameters required to describe large multicomponent aqueous systems.

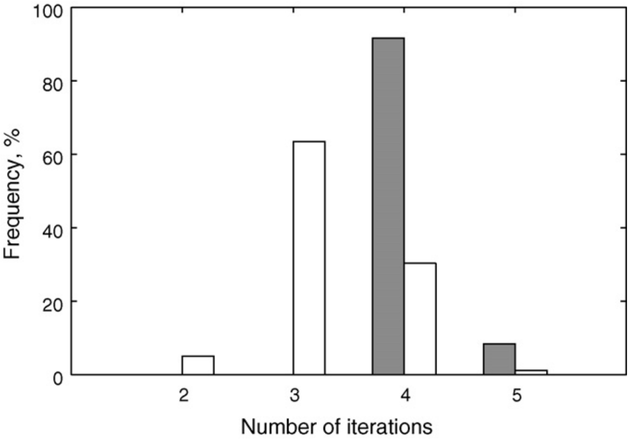

Fig. 4. The number of iterations to achieve convergence.

The convergence of the present algorithm will improve if better starting estimates of the binary concentrations can be found. The approximation that the osmotic coefficients for each binary electrolyte are equal is reasonable when no other information is available. On the other hand, when predicting the water activity for the same mixture of electrolytes at different concentrations many times in succession, the rate of convergence can be greatly improved as follows. For a ternary mixture with composition m_1^A, m_2^A, selected as broadly reflective of the composition of the group of mixtures for which the water activity is to be computed, let the corresponding iso-activity concentrations in the binary solutions be m_{10}^A and m_{20}^A. The isopiestic ratio for the solution is given by $h_{12} = (m_{10}^A / m_{20}^A)$.

The isopiestic ratio can be used to provide an improved estimate of the binary concentrations for subsequent predictions of water activity. If the mixture composition is m_1, m_2, the new estimates of binary concentration will be $m_{10} = m_1 + h_{12} m_2$ and $m_{20} = (m_1 + h_{12} m_2)/h_{12}$. The extension of this to n electrolytes is straightforward, viz. let $h_{1i} = (m_{10}^A / m_{i0}^A)$ then $m_{i0} = \sum_{j=1}^{n} h_{1j} m_j / h_{1i}$.

Fig. 4 shows a histogram of the frequency with which convergence is attained for a system of four electrolytes for randomly selected mixture compositions. The filled bars show the convergence frequencies when the initial concentrations are estimated using the concentration and stoichiometry of the mixture components. The white bars show that the convergence behaviour improves when the starting concentration estimates are informed by prior evaluation of the system. In both cases the concentrations for each electrolyte in the mixture were drawn uniformly from the interval (0.3, 1.5) mol kg^{-1}, yielding total solution concentrations in the approximate range 1.2–6.0 mol kg^{-1}.

In cases where the desired mixture concentrations are known in advance, e.g. in the production of look-up tables or comparison with experiment, the evaluations can proceed in order of decreasing water activity, thereby allowing new starting binary concentrations to be calculated using the slope of the previous evaluation, greatly reducing the subsequent number of iterations.

8. Conclusion

In physical terms, there is a unique mixing path with constant water activity between any two binary (single salt in water) electrolyte solutions. When expressed in molal concentrations, this constant water activity mixing path may be linear (i.e. in accord with Zdanovskii's rule) or, to some modest extent, curved. In either case, the present algorithm seeks to find the concentrations of the binary solutions m_{10}, m_{20}, at each end of the particular line which passes through the point corresponding to the mixed solution in question. The required binary solution concentrations are those which, by definition, have identical water activities. Since every other line pivoting through the mixed point must have water activities at the two ends which differ, and indeed which indicate a direction for adjustment, the unique line of constant water activity can be located and, hence, the water activity of the mixed solution rapidly determined.

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Appendix A.

A.1. Primary algorithm for ideal mixing

At each stage in the algorithm the estimated binary concentrations are related to the concentration in the mixture via

$$m_{i0} = \frac{m_i}{p_i} \tag{A.1}$$

The collection of *p* values – one for each solute – is referred to in this paper as the *partition* of the mixture. The ideal mixing condition is seen to be satisfied when $\Sigma p_i = 1$. This formulation is equivalent to others based on conservation of solvent mass.

The algorithm which finds the water activity of the mixture is given by the following steps.

Step 0: Estimate the binary solution concentrations, adhering to the constraint $\Sigma p_i = 1$.
Step 1: Evaluate the water activity for each binary solution at the given concentration.
Step 2: Stop if the water activity calculations have converged to a single value.
Step 3: Estimate new binary concentrations and go to Step 1.

Details of each step of the algorithm are as follows.

A.2. Algorithm Step 0

The initial partition is chosen to reflect the dominance of each solute. If $\bar{\nu}$ denotes the total moles of dissolved ions and molecules in the solution, $\bar{\nu} = \sum \nu_i m_i$, then $p_i = (\nu_i m_i)/\bar{\nu}$, where ν_i is the number of moles of ions or molecules formed when one mole of solute *i* completely dissociates.

This is a reasonable starting point since $\ln a_w \propto \nu_i m_{i0} \phi_{i0}$. Making the approximation that ϕ_{i0}, the osmotic coefficients for the binary solutions, are all equal means that the iso-activity condition is realised when $\nu_i m_{i0} = \text{const}$, as defined by this initial partition.

For a system of symmetric electrolytes this has the effect that the estimated concentrations for the binary solutions will each be equal to the total concentration of the mixture, and this will give the exact answer for solutes whose water activities vary identically with concentration. Of course, the better this initial approximation the faster the algorithm will converge (see Section 7).

A.3. Algorithm Step 1

The water activity of a solution can be obtained from the osmotic coefficient ϕ using the relation

$$\phi = -M_w (\ln a_w) \bar{\nu}^{-1}$$

where $M_w = 55.51\ \text{mol kg}^{-1}$ is the molar concentration of water. For a single electrolyte the water activity is given by

$$\ln a_w = -\frac{\nu_i m_{i0} \phi_{i0}}{M_w} \tag{A.2}$$

The osmotic coefficient for each binary electrolyte solution can be determined, for example, using the Pitzer equations provided the Pitzer coefficients for the electrolyte are known, which is generally the case for binary electrolytes.

A.4. Algorithm Step 2

The algorithm terminates when the water activity values calculated at Step 1 are sufficiently close to one another. A convenient and simple measure of closeness is the range of the water activity values over all binary electrolyte solutions, i.e. $\chi = \max a_w - \min a_w$.

A.5. Algorithm Step 3

The objective is to adjust the concentrations of the binary solutions m_{i0}, so that solutions with high water activity become more concentrated and solutions with low water activity become more dilute. Conceptually, this can be regarded as exchange of solvent between the binary components.

Consider the case of a ternary mixture and let the *k*th solute be the component with the largest water activity, and the *j*th solute have the smallest water activity. The χ value is minimised if the new partition results in these activities being equal, that is

$$a_w(p_k + \delta p_k) = a_w(p_j + \delta p_j)$$

The left hand side of this relation can be expanded in a Taylor's series

$$a_w(p_k + \delta p_k) = a_w(p_k) + \delta p_k \frac{da_w}{dp_k} + O(\delta p_k^2)$$

Equating this result with the analogous expression for $a_w(p_j + \delta p_j)$ gives to first order

$$a_w(p_k) + \delta p_k \frac{da_w}{dp_k} \approx a_w(p_j) + \delta p_j \frac{da_w}{dp_j}$$

Leaving the sum of the partition values unchanged requires $\delta p_k = -\delta p_j$ therefore

$$\delta p_j \approx \frac{a_w(p_k) - a_w(p_j)}{(da_w/dp_k) + (da_w/dp_j)}$$

The derivative of water activity with respect to p_i is found using the relation

$$\frac{da_w}{dp_i} = \left(\frac{da_w}{dm_{i0}}\right)\left(\frac{dm_{i0}}{dp_i}\right)$$

The first derivative on the right hand side can be determined either numerically or analytically from Eq. (A.2). The second is obtained from the definition in Eq. (A.1). The concentration of the solute in the mixture is constant throughout the investigation so it follows that

$$\frac{dm_{i0}}{dp_i} = -\frac{m_i}{p_i^2}$$

The method of binary concentration adjustment outlined above is equivalent to the Newton–Raphson method for finding the solution of a system of equations [34]. To extend the method to multicomponent systems simply requires constructing the Jacobian matrix of partial derivatives and solving for the δp vector at each iteration.

Appendix B.

The relationship for a ternary solution which holds at isopiestic equilibrium with its pure binary components is

$$\bar{\nu}\phi = \nu_1 m_{10}\phi_{10} = \nu_2 m_{20}\phi_{20}$$

where $\bar{\nu} = \nu_1 m_1 + \nu_2 m_2$. Substituting these relations into Eq. (1) yields

$$\Delta = \frac{\bar{\nu}\phi - \nu_1 m_1 \phi_{10} - \nu_2 m_2 \phi_{20}}{\bar{\nu}\phi}$$

Rearranging this equation gives

$$\phi = \frac{\nu_1 m_1 \phi_{10} + \nu_2 m_2 \phi_{20}}{\bar{\nu}(1-\Delta)}$$

As stated in the discussion of Step 0 in Appendix A, the concentrations of the binary solutions should best reflect the dominance of each solute. Using the condition $\nu_1 m_{10} = \nu_2 m_{20} = m\cdot$, substitution into (1) yields

$$1 = \frac{\nu_1 m_1}{m\cdot} + \frac{\nu_2 m_2}{m\cdot} + \Delta$$

or

$$m\cdot = \frac{\bar{\nu}}{1-\Delta}$$

With this result it follows that the initial partition for nonideal mixing is given by

$$p_i = \frac{\nu_i m_i (1-\Delta)}{\bar{\nu}}$$

and the total value of the partition is $\Sigma p_{\mathrm{i}} = 1 - \Delta$. When the deviation can be calculated *a priori* given the mixture composition (as is the case for the simple deviation considered here) the only change to the algorithm occurs when the initial concentration estimates are made.

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