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Published in:
Fluid Phase Equilibria

Link to article, DOI:
[10.1016/j.fluid.2022.113441](https://doi.org/10.1016/j.fluid.2022.113441)

Publication date:
2022

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Nikolaidis, I. K., Novak, N., Kontogeorgis, G. M., & Economou, I. G. (2022). Rigorous Phase Equilibrium Calculation Methods for Strong Electrolyte Solutions: The Isothermal Flash. *Fluid Phase Equilibria*, 558, Article 113441. <https://doi.org/10.1016/j.fluid.2022.113441>

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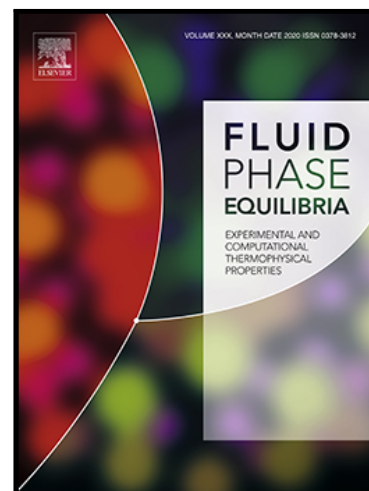
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PII: S0378-3812(22)00066-8
DOI: <https://doi.org/10.1016/j.fluid.2022.113441>
Reference: FLUID 113441



To appear in: *Fluid Phase Equilibria*

Received date: 8 January 2022
Revised date: 2 March 2022
Accepted date: 7 March 2022

Please cite this article as: Ilias K. Nikolaidis , Nefeli Novak , Georgios M. Kontogeorgis , Ioannis G. Economou , Rigorous Phase Equilibrium Calculation Methods for Strong Electrolyte Solutions: The Isothermal Flash, *Fluid Phase Equilibria* (2022), doi: <https://doi.org/10.1016/j.fluid.2022.113441>

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Rigorous Phase Equilibrium Calculation Methods for Strong Electrolyte Solutions: The Isothermal Flash

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For publication in *Fluid Phase Equilibria*

February 2022

Abstract

New algorithms for vapor – liquid (VLE) and liquid - liquid (LLE) equilibrium calculations at constant temperature, pressure and feed phase composition (PT flash), with application to mixtures containing fully dissociating electrolytes are presented. A new approach is proposed and is rigorously derived by treating phase equilibrium as a minimization problem of the Gibbs free energy, while utilizing the electro-neutrality condition as a constraint. In this way, an augmented function (Lagrange function) is formulated which serves as the basis for the equations that govern phase equilibrium. It is shown that the Lagrange multiplier which corresponds to the electro-neutrality constraint has theoretical meaning and direct relation to the electrostatic potential difference between inhomogeneous phases. Based on the new approach, named Electrochemical Ionic Approach (EIA), two new numerical methods are presented; a successive substitution method similar to the classical Rachford-Rice method and a second-order one, which is based on Newton's method. The new algorithms are general and can be readily applied to mixtures of multiple solvents and one or multiple salts without any modifications. Finally, the Mean Ionic Approach (MIA) for mixtures with multiple solvents and only one salt is discussed in detail and a successive substitution and a second-order method are formulated. Moreover, the MIA is formally extended and presented for mixtures of multiple solvents and multiple salts. All the resulting methods are applied to mixtures with multiple solvents and one or multiple strongly dissociating electrolytes. The performance and technical details of each method are discussed and compared. The calculations are performed with the electrolyte Statistical Associating Fluid Theory with the Mie potential of variable range (eSAFT-VR Mie) equation of state but the proposed methods are general and could be used with any other thermodynamic model.

1. Introduction

Phase equilibrium calculations are an integral part of computer aided process design in a vast number of engineering applications, such as chemical process design, two-phase flow simulation,¹ compositional reservoir simulation, prediction of scale formation, etc. In these simulations, usually a large number of phase equilibrium calculations are performed and they regularly constitute the most computationally intensive part, especially when complex equations of state (EoS) are used. Furthermore, phase equilibrium calculation failure can lead to erroneous results or even complete breakdown of the whole simulation. Consequently, robustness and computational efficiency of the phase equilibrium algorithm are of imperative importance.

Phase equilibrium is usually formulated as an optimization problem²⁻⁸ or as a problem of nonlinear equations.⁹⁻¹² The most important and widespread phase equilibrium calculation is probably the isothermal flash (PT flash),³ i.e., the computation of the composition of two or more coexisting phases and the amount of each one at specified temperature (T), pressure (P) and overall composition of an unstable mixture. Since the isothermal flash is a type of phase equilibrium calculation, it can also be treated mathematically either as a Gibbs free energy minimization problem or as a set of nonlinear equations. The formulation as a nonlinear equation set can be done by solving simultaneously the isofugacity (or chemical potentials) relations together with the constraints which are comprised by the material balances and the mole fractions summation.^{9,12,13} In this category fall also the methods that solve the constraints (material balance, summation of mole fractions) internally, using an estimate of the K -values and then update them in an outer loop.^{3,10,14} A third case of equation solving methods are those that solve the isofugacity equations, which are the components of the gradient of the total Gibbs free energy of the system with respect to the number of moles per component, but perform a change of independent variables, in order to obtain better convergence properties.^{5,12,15} Gibbs free energy minimization has also been studied and used extensively as an alternative to equation solving techniques.^{3,6,8,16,17}

The different algorithmic formulations and treatment of the isothermal flash calculation mentioned above are applied to mixtures of components that do not contain ionic species. The inclusion of electrolytes in a mixture requires certain modifications in the computational procedure. Modeling of vapor-liquid (VLE) and liquid-liquid equilibrium (LLE) of electrolyte mixtures with excess Gibbs free energy models and EoS is not a new

subject. However, the literature dedicated to computational methods and the specific details regarding the application and performance of relevant algorithms is very scarce.

Electrolytes are traditionally categorized as strong or weak, depending on the degree of dissociation. Weak electrolytes dissociate partially and therefore, in the mixture, ions are in chemical equilibrium with the undissociated salt. Solving phase equilibria for weak salts requires methodologies for simultaneous physical and chemical equilibria. Recently, Tsanas et al.¹⁸ extended two non-stoichiometric methods that minimize the total Gibbs free energy to determine multiphase, physical and chemical equilibrium of electrolyte solutions and showed that the electro-neutrality condition is implicitly satisfied when the material balance is satisfied. He also introduced a reactive flash algorithm that minimizes the Gibbs free energy taking into account the charge/electric potential contribution to the Gibbs energy to allow application to multiple phases containing electrolytes.¹⁹

Strong electrolytes on the other hand are assumed to dissociate fully and, therefore, the electrolyte phases contain only ions and no salt. Consequently, calculation of phase equilibrium for mixtures that contain strong electrolytes can be formulated as a physical equilibrium problem. In terms of mathematical formulation, the basic difference from traditional non-electrolyte phase equilibrium methodologies is the requirement that all phases have to be electro-neutral, which adds additional constraints to the problem, as will be explained in Section 3. The literature on methodologies for the calculation of phase equilibria of electrolyte solutions is scarce, and mostly limited to single salts. Most researchers²⁰⁻²⁸ utilize the concept of the Mean Ionic Approach (MIA), which will be discussed in detail in Section 2 where the available literature on electrolyte phase equilibrium calculation methods is presented and discussed. Furthermore, in Section 4, our implementation of the MIA for an isothermal flash calculation is formally presented and formulated as two different methodologies (first and second order). The MIA is also extended to mixtures with multiple salts, which requires significant work because of the low availability of open literature dedicated to the subject.

Additionally, in this work, a new framework for calculating phase equilibrium in electrolyte solutions is mathematically derived and its theoretical origin is justified. This new method is referred to as Electrochemical Ionic Approach (EIA). Two algorithms (first and second-order) are formally presented based on the new approach and their computational performance is assessed. It is shown that this framework can be applied to mixtures with multiple solvents and multiple salts without any modifications. The EIA (both as first and second order) is compared with the MIA as formulated in this work. Finally, we also

demonstrate how the same methods that were constructed for LLE can be applied to VLE calculations without the need of constraining the ions to the liquid phase by forcing their K -values arbitrarily to zero.

2. Existing phase equilibrium calculation methods for electrolyte solutions

In this section, the existing approaches for phase equilibrium methods in electrolyte solutions are briefly presented and discussed. LLE and VLE calculations in electrolyte solutions can be treated in a unified framework or as two different mathematical problems. This stems from the need to enforce the electro-neutrality constraint. In VLE calculations, the inclusion of the electro-neutrality constraint in the equation set can be overcome. In this case, traditional phase equilibrium methods can be used if the ions are restricted to the liquid phase,^{29–32} which is a valid assumption since the vapor phase does not contain any ions in most cases of practical interest. The same assumption has been made for the oil phase when calculating LLE of water with n-alkanes under salinity,³³ due to the very low dielectric constant of the nonpolar n-alkane and the very low mutual solubility of the two species. This can be done for example by setting the K -values (for VLE $K_i = \frac{y_i}{x_i}$, for LLE $K_i = \frac{w_i}{x_i}$) of the ionic species equal to zero. In this way, if the feed phase of molar composition (\mathbf{z}) is electro-neutral, then the liquid phase with composition (\mathbf{x}) and the vapor phase with composition (\mathbf{y}) or the second liquid phase with composition (\mathbf{w}) are going to be electro-neutral as well. However, we believe that, in the case of phase equilibrium, the ions should not be constrained to specific phases; on the contrary, they must be free to distribute between all phases and the relative permittivity of the model should be the reason the ions prefer the more polar phase. Our view falls in line with Schreckenberget al.²⁷ who applied the MIA in VLE calculations without restricting the ions to the liquid phase. This approach offers the flexibility of using a unified framework for phase equilibrium calculations regardless the type of phases involved.

Regarding the calculation of LLE, most researchers^{20–28} utilize the concept of the MIA. That is, since each bulk phase is, on average, electrically neutral, ions must move between phases in neutral combinations.³⁴ These combinations typically correspond to the actual salts. According to this methodology the mean values for the mole fractions, x_{\pm} , molality, m_{\pm} , fugacity coefficients, $\hat{\phi}_{\pm}$, and activity coefficients, γ_{\pm} , expressed in different reference states, namely molal, γ_{\pm}^m , or unsymmetrical, γ_{\pm}^* are used:

$$x_{\pm} = (x_+^{\nu_+} x_-^{\nu_-})^{1/\nu} \quad (1)$$

$$m_{\pm} = (m_+^{\nu_+} m_-^{\nu_-})^{1/\nu} \quad (2)$$

$$\hat{\phi}_{\pm} = (\hat{\phi}_+^{\nu_+} \hat{\phi}_-^{\nu_-})^{1/\nu} \quad (3)$$

$$\gamma_{\pm} = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/\nu} \quad (4)$$

where $\nu = \nu_+ + \nu_-$; ν_+ denotes the stoichiometric coefficient of the cation and ν_- of the anion. The chemical potential of the salt, which is formed by a cation-anion pair is given by:

$$\mu_S = \nu_+ \mu_+ + \nu_- \mu_- \quad (5)$$

Phase equilibrium, based on the MIA, requires equality of chemical potentials between phases for each neutral component, i.e., regular molecular compounds and salts (cation-anion pairs). Chemical potential equality can be converted to the isofugacity or iso-activity condition, depending on which property is more easily accessible from a particular model. The studies that use an EoS as thermodynamic model utilize the isofugacity criterion^{20–23,27} for phase equilibrium (Eq. 6), while those using activity coefficient models use the iso-activity condition^{24–26,28} instead (Eq. 7):

$$w_{\pm} \hat{\phi}_{\pm}^a = x_{\pm} \hat{\phi}_{\pm}^b \quad (6)$$

$$m_{\pm}^a \gamma_{\pm}^a = m_{\pm}^b \gamma_{\pm}^b \quad (7)$$

where a and b refer to the two phases in equilibrium. When the asymmetric mean ionic activity coefficients are used, all species must have the same reference state in both liquid phases, therefore an appropriate conversion is need.^{21,35} Such a conversion is not necessary when the symmetric activity coefficient²⁴ or fugacity coefficients are used instead.

2.1. Single Electrolytes

It is possible to incorporate the MIA into the existing isothermal flash calculation methodologies (for non-electrolyte solutions) to solve for electrolyte LLE with EoS. The isothermal flash calculation requires the minimization of Gibbs free energy under the constraint that the material balance is satisfied as well. This translates to chemical potential equality (isofugacity or iso-activity) with simultaneous material balance satisfaction. The material balance formulation in this case requires particular attention, because it must be formulated based on the true ionic composition of the mixture, in order for the mole fractions of the molecular components to be calculated correctly. Münster³⁶ in Chapter XI: “Electrochemical systems”, discusses in relative detail the fact that the mean mole fractions of

the salts and of the molecular components in a mixture do not add up to 1. Moreover, most thermodynamic models use the true ionic composition to calculate the various properties, such as fugacity coefficients. In order to solve the material balance based on the true ionic composition, the K -values of the ions should be used. For two phases in equilibrium, the respective K -values and fugacity coefficients are calculated based on the mean ionic values (those of the salt):

$$K_+ = \frac{w_+}{x_+} = K_- = \frac{w_-}{x_-} = K_{\pm} = \frac{w_{\pm}}{x_{\pm}} \quad (8)$$

$$K_{\pm} = \frac{\hat{\phi}_{\pm}^b}{\hat{\phi}_{\pm}^a} \quad (9)$$

where w is the mole fraction of phase a , x is the mole fraction of phase b , and $\hat{\phi}_{\pm}$ is calculated from Eq. 3. Eqs. 8 and 9 are a direct consequence of the electro-neutrality constraint and ensure the correct analogy between the cation and the anion of a neutral pair in each coexisting phase. In other words, the electro-neutrality constraint is formally eliminated from the equations that have to be satisfied at equilibrium, by applying Eqs. 8 and 9. The material balance can be solved simultaneously or in a nested loop (depending on the method) and takes into account both molecular and ionic species. The true ionic composition is then calculated from the respective K -values that satisfy the material balance. In Section 4, the Rachford-Rice method modified for electrolyte mixtures and a second order calculation method are going to be presented in detail based on the MIA.

Another interesting way to take into account the electro-neutrality constraint in the Rachford-Rice equations was proposed by Ahmed³⁷ who adopted the approach of Pfennig and Schwerin.³⁸ Pfennig and Schwerin used modified partition coefficients that take into account the electrostatic potential difference between two inhomogeneous phases, following the work of Albertsson.³⁹ Ahmed²⁶ proposed a Rachford-Rice type method, in which modified fugacity coefficients are utilized, as shown in Eq. 10:

$$\ln \tilde{\phi}_i = \ln \hat{\phi}_i + \frac{\psi \mathcal{F} q_i}{RT} \quad (10)$$

where $\hat{\phi}_i$ is the fugacity coefficient without taking into account the electrostatic potential (what is traditionally calculated by EoS), ψ is the electrostatic potential of the respective phase, q_i the electrovalence of species i (positive for cations, negative for anions), and \mathcal{F} is Faraday's constant. Using this approach, the K -values of each component are calculated using the fugacity coefficient of phase a , $\hat{\phi}_i^a$, and phase b , $\hat{\phi}_i^b$:

$$\ln \tilde{K}_i = \ln \tilde{\varphi}_i^b - \ln \tilde{\varphi}_i^a = \ln \frac{\hat{\varphi}_i^b}{\hat{\varphi}_i^a} + \frac{(\psi^b - \psi^a)\mathcal{F}q_i}{RT} \quad (11)$$

For a single salt $C_{v_+}A_{v_-}$ the condition of electro-neutrality states that the K -values of the two ionic species C and A , \tilde{K}_i , should be equal (as stated in Eq. 8 in the mean ionic approach). Then, the electrostatic potential difference can be calculated by Eq. 12, which is known as the Albertsson equation^{38,39}:

$$\Delta\psi = \psi^b - \psi^a = \frac{RT}{\mathcal{F}(q_- - q_+)} (\ln K_- - \ln K_+) \quad (12)$$

Substitution of Eq. 12 into Eq. 10 along with some rearrangement finally yields the modified fugacity coefficients³⁷:

$$\ln \tilde{\varphi}_i = \ln \hat{\varphi}_i + \frac{q_i}{q_- - q_+} \ln \frac{\hat{\varphi}_+}{\hat{\varphi}_-} \quad (13)$$

This expression can be easily implemented in traditional phase equilibrium calculation methods, such as the classical Rachford-Rice method. Ahmed³⁷ used this approach for LLE calculation of mixed solvents and one salt only.

Last but not least, in the thesis of Maribo-Mogensen⁴⁰, another way of utilizing traditional phase equilibrium calculation methods has been presented but was used only for single salt solutions. Maribo-Mogensen introduced neutral salts as apparent components, and used the apparent fugacity coefficient, $\hat{\varphi}_{app,i}$. This method is an analogy of the chemical reaction equilibrium as described in the book of Michelsen and Mollerup.⁴¹

$$\ln \hat{\varphi}_{app,i} = -\ln \frac{x_{app,i}P}{P_0} + \sum_j v_{ij} \ln \frac{x_j \hat{\varphi}_j P}{P_0} \quad (14)$$

where $x_{app,i}$ is the apparent mole fraction, x_j is the true (ionic) mole fraction, $\hat{\varphi}_j$ is the ionic fugacity coefficient and v_{ij} the stoichiometric coefficient of ion j in salt i . The apparent mole fractions, $x_{app,i}$, are calculated using a salt based composition in terms of mole numbers, ns_i , as:

$$x_{app,i} = ns_i / \sum_k^{solvents+salts} ns_k \quad (15)$$

$$x_j = \sum_i^{salts} v_{ij} ns_i / \left(\sum_k^{solvents} ns_k + \sum_l^{salts} v_{kl} ns_k \right) \quad (16)$$

2.2. Multiple Electrolytes

The discussion until now has been restricted to mixtures of one or multiple solvents, but only one salt. To our knowledge, there are not any modeling research studies available in the open literature that deal with mixtures of multiple strong electrolytes in the context of LLE. In the work of Schreckenberget al.²⁷, vapor pressure calculations with the MIA for aqueous solutions with multiple salts were showcased. A complicating factor associated with the MIA, is that when more than one salt are present in a mixture, a suitable combination of cation-anion pairs must be selected to perform the calculation. The important question that is raised at this point is which cation-anion pairs should be selected. For example, for a mixture of two solvents that contains Na^+ , Cl^- , K^+ , Br^- , four possible salts can be formed (NaCl, NaBr, KCl and KBr). Wang et al.²⁴ state that the MIA can be applied to mixtures of multiple salts, provided that a linearly independent set of cation-anion pairs is defined, which typically corresponds to the actual salts. Furthermore, the authors state that once the equality of chemical potentials is satisfied for a linearly independent set of cation-anion combinations, it is also satisfied for any other combination. However, the authors do not elaborate on how to test for linear independence and have not presented a formal extension of the MIA to mixtures containing multiple salts.

The dependency between the mean fugacity or activity coefficients of electrolytes in mixtures containing several salts that have certain ionic species in common is also discussed by Münster [31] in Chapter XI: “Electrochemical systems” and is a direct consequence of Eqs. 3 and 4. Furthermore, although we have made the assumption that salts dissociate fully to their respective ions; the dissociation reactions (or equivalently the chosen set of salts, since $C_{v_+}A_{v_-} \rightarrow v_+C^{q_+} + v_-A^{q_-}$) must be linearly independent,⁴¹ i.e. none of the reactions may be linear combinations of the others. Hence, phase equilibrium calculation with the MIA, when treating mixtures of multiple salts, requires to take into account a suitable linearly independent combination of salts.

In Section 4.2, a method for testing whether a combination of salts is linearly independent will be provided; a stoichiometric matrix of the electrolyte system can be constructed and checked for full rank as a test for linear independence. Furthermore, in the case of multiple salts Eqs. 8 and 9 are not valid, since they were derived based on the assumption of a single electrolyte. Instead, the electro-neutrality constraint must be taken into account explicitly in the equation set. For the mixture mentioned above, only three of the four possible salts (NaCl, NaBr, KCl and KBr) must be taken into account for the equilibrium calculation.

An extension of the MIA to mixtures containing multiple salts was presented by Grossmann and Maurer⁴². In their publication, the authors tackled important considerations, regarding the number of phase equilibrium equations that need to be taken into account when multiple salts can be formed in a mixture and the need to explicitly account for the electro-neutrality constraint in the equation set, when calculations are performed at constant temperature and pressure. The authors proved the important fact that $N_{Ions} - 1$ equilibrium relations are needed for neutral cation-anion combinations, by utilizing the electro-neutrality constraint to render the mole numbers of one ion of the mixture dependent variable. However, the independent set of equations that they proposed subsequently for the solution of the phase equilibrium problem included again the electro-neutrality condition, which mathematically at least comes in contrast with the previous elimination of one variable using the same equation. Finally, the authors mention that the only restriction in forming the set of neutral cation-anion combinations is that each ion must appear in at least one neutral salt. However, the authors did not present any formal justification. We will show later on that the claim can be formally justified by the use of the stoichiometric matrix of the electrolyte system.

Last but not least, the model of Albertsson can in principle be extended to mixtures that include multiple salts, as shown by Pfennig and Schwerin,³⁸ but the calculation of $\Delta\psi$ is not analytical and requires numerical solution of the electro-neutrality condition (expressed in K -values) together with Eq. 11. This extension however was only theoretically discussed and no formal extension or any calculations have been provided.

3. New Framework for Phase Equilibria: The Electrochemical Ionic

Approach (EIA)

3.1. Derivation of Working Equations

As it has already been mentioned in the Introduction, calculation of a stable thermodynamic equilibrium state corresponds to finding the global minimum of Gibbs free energy, when temperature and pressure are both fixed. The two-phase or the multiphase PT flash calculations are such cases, in which we seek to find the global minimum of the total Gibbs free energy, which is the sum of the Gibbs free energies of the individual phases that comprise the system. For non-reactive systems, the problem is constrained by the material balances if written in terms of mole numbers or the material balances and the mole fractions summation equations if mole fractions and molar phase fractions are used.

When charged species (ions) are present in a mixture, the electro-neutrality condition must be satisfied as well. In this work, we are concerned only with systems in which electrolytes fully dissociate into their respective ionic components and thus a mixture contains only neutral molecular species and ions. For a mixture of N_C components (molecular species + ionic species), the electro-neutrality condition can be written as:

$$\sum_{i=1}^{N_C} q_i n_i = 0 \quad (17)$$

where q_i is the electrovalency (positive or negative) and n_i the mole number of component i . Of course, for neutral molecular species $q_i = 0$. When two or more phases are in equilibrium, the electro-neutrality condition imposes an extra constraint that must be accounted for. At this point an important question to be addressed is whether the electro-neutrality constraint has to be applied to each one of the coexisting phases. We prove in Appendix A that when N_P phases are in equilibrium, $N_P - 1$ electro-neutrality conditions are required. For two phases in equilibrium the electro-neutrality condition must be applied only to one of the coexisting phases; the other phase will be electro-neutral as well.

The electro-neutrality condition can be imposed as a constraint in the minimization of the Gibbs free energy of the system with the use of Lagrange multipliers. The material balance constraints can be formally eliminated by setting:

$$n_i^b = z_i - n_i^a; \quad i = 1, 2 \dots N_C \quad (18)$$

The Lagrange function takes the form:

$$\mathcal{L}(\mathbf{n}^a, \lambda_a) = G(\mathbf{n}^a)^{total} + \lambda_a \sum_{j=1}^{N_C} q_j n_j^a \quad (19)$$

The first order optimality conditions that correspond to a stationary point of the Lagrangian are:

$$\begin{aligned} \frac{\partial \mathcal{L}(\mathbf{n}^a, \lambda_a)}{\partial \mathbf{n}^a} &= 0 \\ \frac{\partial \mathcal{L}(\mathbf{n}^a, \lambda_a)}{\partial \lambda_a} &= 0 \end{aligned} \quad (20)$$

The total Gibbs free energy is:

$$G(\mathbf{n}^a)^{total} = G^a + G^b = \sum_{i=1}^{N_C} n_i^a \mu_i^a(T, P, \mathbf{w}) + \sum_{i=1}^{N_C} n_i^b \mu_i^b(T, P, \mathbf{x}) \quad (21)$$

where \mathbf{w} and \mathbf{x} are the molar composition vectors of the two phases.

$$\frac{\partial G(\mathbf{n}^a)^{total}}{\partial n_i^a} = \frac{\partial G^a}{\partial n_i^a} + \frac{\partial G^b}{\partial n_i^a} = \frac{\partial G^a}{\partial n_i^a} - \frac{\partial G^b}{\partial n_i^b} = \mu_i^a(T, P, \mathbf{w}) - \mu_i^b(T, P, \mathbf{x}) \quad (22)$$

By combining Eqs. 19 - 22 , the first order optimality conditions become:

$$\frac{\partial \mathcal{L}(\mathbf{n}^a, \lambda_a)}{\partial n_i^a} = \mu_i^a(T, P, \mathbf{w}) - \mu_i^b(T, P, \mathbf{x}) + \lambda_a q_i = 0; \quad i = 1, 2 \dots N_C \quad (23)$$

$$\frac{\partial \mathcal{L}(\mathbf{n}^a, \lambda_a)}{\partial \lambda_a} = \sum_{j=1}^c q_j n_j^a = 0$$

Eq. 23 is the equation set that governs two-phase equilibrium at constant temperature and pressure when charged species are present in a mixture and no reactions take place (electrolytes are fully dissociated into their respective ionic components). These equations are the basis for the EIA.

3.2. Theoretical Meaning of the Lagrange Multiplier

In this section, the equations derived for the phase equilibrium problem when ions are present in a mixture (Eq. 23) are going to be connected with the formal macroscopic thermodynamic treatment of electrochemical systems, according to Münster³⁶ in Chapter XI: “Electrochemical systems” as well as on relevant publications from Guggenheim.^{43,44} Similarly to the previous section, the analysis of Münster assumes that electrolytes are fully dissociated and thus the solution contains only neutral molecules and ions. As pointed out by Münster³⁶, if electrostatic potential differences occur (this is possible only in heterogeneous systems) the electro-neutrality condition is no longer strictly applicable. However, the deviations are so small, that for any potential differences, they lie far below the limits of any experimental data. This fact justifies an approximation which constitutes the formal basis for the thermodynamic treatment of electrochemical systems.

Following Münster³⁶, the fundamental thermodynamic equations must be modified and generalized accordingly in order to derive suitable phase equilibrium relations that describe electrochemical systems. In this sense, the variation of internal energy can be written as:

$$\delta\tilde{U} = \delta U + \delta U^e \quad (24)$$

where \tilde{U} is the generalized internal energy that is comprised of two parts, the electrical one being U^e and the non-electrical one being U . The electrostratic relationship for the variation of U^e of a conductor can be calculated as (Appendix B):

$$\delta U^e = \psi \delta e = \psi \mathcal{F} \sum_{i=1}^{N_c} q_i \delta n_i \quad (25)$$

where \mathcal{F} is the Faraday constant, ψ is the electric potential, q_i is the electrovalency and n_i the mole numbers of component i . The fundamental equation for the internal energy becomes:

$$d\tilde{U} = TdS - PdV + \sum_{i=1}^{N_c} (\mu_i + \psi \mathcal{F} q_i) dn_i \quad (26)$$

and

$$\tilde{\mu}_i = \mu_i + \psi \mathcal{F} q_i \quad (27)$$

The quantity $\tilde{\mu}_i$ was suggested by Guggenheim⁴³ to be called “electrochemical” potential. For electrically charged species, μ_i in Eq. 27, is the sum of the classical contribution due to short-range intermolecular forces, association, coulombic interactions, etc., in other words the chemical potential as is calculated by an electrolyte EoS or activity coefficient model, and an electric contribution, $\psi \mathcal{F} q_i$.⁴¹

The decomposition of $\tilde{\mu}_i$ in two terms, as shown in Eq. 27, and their physical significance has been discussed thoroughly in the literature but it remains a matter of controversy. Guggenheim claimed that the equilibrium of an ion is determined by $\tilde{\mu}_i$ that has the real physical significance, while the decomposition into μ_i and $\psi \mathcal{F} q_i$ has no physical significance.⁴³ The justification for this statement stems from the work of Gibbs (quotation in a letter of Gibbs, as reported by Guggenheim⁴⁴) and Guggenheim⁴³ that both pointed out that the electric potential difference between two points of different media is not a measurable quantity. A direct consequence is that the chemical potential of a single ion is not a measurable quantity as well, because of the existence of liquid junction potentials, whose value in turn cannot be calculated without knowing the ionic chemical potentials that one wishes to measure. However, in order to fall in line with the view of Brønsted who attached significant importance into the decomposition of the electrochemical potential, in a subsequent publication,⁴⁴ Guggenheim revisited the subject. He concluded that the electric

potential difference between two phases in equilibrium can be seen as a measure of the asymmetrical distribution of electric charge between the two phases. However, no experiment could be performed at that point that would be able to measure this kind of electric potential difference and consequently the chemical potential, activity or activity coefficient of an individual ion.

Recently, individual ion activity coefficients have been published in the literature by Vera^{45,46} and others.^{47,48} In their paper, Wilczek-Vera and Vera⁴⁹ presented a brief historical review of the feasibility of activity of individual ions measurements. In the same paper, they claimed that this quantity can actually be obtained by performing continuous runs in electrochemical cells formed by ion selective electrodes and a standard single junction reference electrode. However, their work has been strongly criticized by Malatesta,^{50,51} who claims that the values reported as individual ion activity coefficients are not accurate, but rather they are “an artifact of the starting hypotheses on the ion activity coefficients”.

In any case, measurable or not, the use of either $\tilde{\mu}_i$ or its decomposed form (Eq. 27) can be mathematically employed to perform phase equilibrium calculations with identical final results. For two phases (a and b) in equilibrium, Eq. 26 leads to the following conditions (electro-neutrality condition must be satisfied as well):

$$T^a = T^b \quad (28)$$

$$p^a = p^b \quad (29)$$

$$\tilde{\mu}_i^a = \tilde{\mu}_i^b; i = 1, 2 \dots N_C \quad (30)$$

At constant temperature and pressure, Eqs. 28 and 29 are satisfied by definition. By decomposing the electrochemical potentials in Eq. 30 we get:

$$\mu_i^a - \mu_i^b + \mathcal{F}(\psi^a - \psi^b)q_i = 0; i = 1, 2 \dots N_C \quad (31)$$

By comparing Eq. 31 with Eq. 23 it is evident that:

$$\lambda_a = \mathcal{F}(\psi^a - \psi^b) \quad (32)$$

In conclusion, the phase equilibrium relations derived by mathematically treating the problem as a constrained minimization are verified and are equivalent to the equations occurring by the formal thermodynamic treatment of electrochemical systems. At the

solution, the value of the Lagrange multiplier is equal to the Faraday constant multiplied by the electric potential difference of the two phases at equilibrium.

3.3. Numerical Methods

In order to solve the EIA numerical methods are formed, which are easily applied in connection with EoS. Eqs. 19 and 23 are expressed in terms of fugacities:

$$\mathcal{L}(\mathbf{n}^a, \lambda) = \frac{G(\mathbf{n}^a)^{total}}{RT} + \lambda \sum_{j=1}^{N_c} q_j n_j^a \quad (33)$$

where $\lambda = \frac{\lambda_a}{RT}$.

The first order optimality conditions become:

$$\frac{\partial \mathcal{L}(\mathbf{n}^a, \lambda)}{\partial n_i^a} = \ln \hat{f}_i^a(T, P, \mathbf{w}) - \ln \hat{f}_i^b(T, P, \mathbf{x}) + \lambda q_i = 0; \quad i = 1, 2 \dots N_c \quad (34)$$

$$\frac{\partial \mathcal{L}(\mathbf{n}^a, \lambda)}{\partial \lambda} = \sum_{j=1}^{N_c} q_j n_j^a = 0$$

where \hat{f}_i is the fugacity of component i in the respective phase. The solution of the $N_c + 1$ equations expressed in Eq. 34 can be performed by applying optimization methods or by treating them as a set of non-linear equations. Regarding the optimization approach, the stationary point of the Lagrange function is a saddle point and as a result without a reformulation, many numerical optimization techniques such as the method of the gradient descent cannot be applied. Newton's method without explicit line search could be applied using as independent variables (\mathbf{n}^a, λ) . This method would be similar to the Gibbs free energy minimization method proposed in Chapter 10 by Michelsen and Mollerup.⁴¹ It has been shown by Petitfrere and Nichita^{12,15} that the use of K -values as independent variables combined with Newton's method for non-linear systems leads to a better conditioned Jacobian matrix as compared to the respective Hessian when component mole numbers are employed. A matrix with lower condition number usually ensures a more robust method. The authors have also stated that the robustness of the Gibbs free energy minimization method diminishes close to the phase boundaries, but when convergent, the method needs a lower number of iterations compared to the use of K -values as independent variables. Based on our own numerical experiments for mixtures with molecular components only, we can verify that the Gibbs free energy minimization method converges in less iterations than the K -value method, showing quadratic convergence rate (when sufficiently close to the solution) at points not close to the phase boundary. On the other hand, for numerical solutions at phase fractions

close to 0 or 1 (near the phase boundaries), the two methods need similar number of iterations for convergence, with the K -value method being more robust. The convergence rate of the K -value method is usually super-linear, thus converging faster than a first order method (linear).

In this work, Eqs. 34 are treated as a non-linear system of equations and two numerical methods are proposed. A second-order one based on Newton's method for non-linear systems (analogous to the K -value method discussed previously) and a successive substitution (first-order method) one which is similar to the Rachford-Rice¹⁴ method for mixtures without ionic species. The non-linear equation set for the second-order method takes the form:

$$g_i = \ln K_i + \ln \hat{\varphi}_i^a(T, P, \mathbf{w}) - \ln \hat{\varphi}_i^b(T, P, \mathbf{x}) + \lambda q_i = 0; \quad i = 1, 2 \dots N_C \quad (35)$$

$$g_{N_C+1} = \sum_{l=1}^{N_C} z_l \frac{K_l - 1}{1 - \beta + \beta K_l} = 0 \quad (36)$$

$$g_{N_C+2} = \sum_{l=1}^{N_C} q_l w_l \beta = 0 \quad (37)$$

where $\hat{\varphi}_i$ is the fugacity coefficient of component i in the respective phase, $K_i = \frac{w_i}{x_i}$, $n_i^a = w_i \beta$ and β is the molar phase fraction. The vector of independent variables is $\mathbf{X} = (\ln K_1, \dots, \ln K_{N_C}, \beta, \lambda)$. The elements of the Jacobian matrix for the equation set mentioned above are:

$$J_{ij} = \frac{\partial g_i}{\partial \ln K_j} = \delta_{ij} + (1 - \beta) \frac{w_j x_j}{z_j} \frac{\partial \ln \hat{\varphi}_i^a(T, P, \mathbf{w})}{\partial w_j} + \beta \frac{w_j x_j}{z_j} \frac{\partial \ln \hat{\varphi}_i^b(T, P, \mathbf{x})}{\partial x_j}; \quad i, j = 1, 2 \dots N_C \quad (38)$$

$$J_{i, N_C+1} = \frac{\partial g_i}{\partial \beta} = \sum_{l=1}^{N_C} \frac{w_l}{z_l} \left(x_l \frac{\partial \ln \hat{\varphi}_i^b(T, P, \mathbf{x})}{\partial x_l} - w_l \frac{\partial \ln \hat{\varphi}_i^a(T, P, \mathbf{w})}{\partial w_l} \right); \quad i = 1, 2 \dots N_C \quad (39)$$

$$J_{i, N_C+2} = \frac{\partial g_i}{\partial \lambda} = q_i; \quad i = 1, 2 \dots N_C \quad (40)$$

$$J_{N_C+1, j} = \frac{\partial g_{N_C+1}}{\partial \ln K_j} = K_j \frac{z_j}{(1 - \beta + \beta K_j)^2}; \quad j = 1, 2 \dots N_C \quad (41)$$

$$J_{N_C+1, N_C+1} = \frac{\partial g_{N_C+1}}{\partial \beta} = - \sum_{l=1}^{N_C} z_l \frac{(K_l - 1)^2}{(1 - \beta + \beta K_l)^2} \quad (42)$$

$$J_{N_C+1, N_C+2} = \frac{\partial g_{N_C+1}}{\partial \lambda} = 0 \quad (43)$$

$$J_{N_C+2, j} = \frac{\partial g_{N_C+2}}{\partial \ln K_j} = q_j \beta (1 - \beta) \frac{w_j x_j}{z_j}; \quad j = 1, 2 \dots N_C \quad (44)$$

$$J_{N_C+2, N_C+1} = \frac{\partial g_{N_C+2}}{\partial \beta} = \sum_{l=1}^{N_C} q_l \left(\frac{x_l - z_l}{\beta} + w_l \right) \quad (45)$$

$$J_{N_C+2, N_C+2} = \frac{\partial g_{N_C+2}}{\partial \lambda} = 0 \quad (46)$$

The Newton iteration becomes:

$$\mathbf{X}^{(k+1)} = \mathbf{X}^{(k)} + \delta \mathbf{X}^{(k)} \quad (47)$$

$$\mathbf{J}^{(k)} \delta \mathbf{X}^{(k)} = -\mathbf{g}^{(k)} \quad (48)$$

After every iteration, the values of the component mole fractions in each phase are retrieved using:

$$x_i = \frac{z_i}{1 - \beta + \beta K_i} \quad (49)$$

$$w_i = \frac{K_i z_i}{1 - \beta + \beta K_i} \quad (50)$$

The fugacity coefficients are then reevaluated using a thermodynamic model (in this work an EoS) and the procedure is repeated until convergence. The proposed numerical method can be converted to a first-order one by setting the composition derivatives of the fugacity coefficients equal to zero. This can be done for a couple of iterations at the beginning, since first-order methods are usually less prone to divergence, and then convert to the full second-order for faster convergence. More details are going to be given in Section 6. It has to be kept

in mind that setting the composition derivatives of the fugacity coefficients equal to zero results in a method having exactly the same convergence rate as the successive substitution approach, since both are based on the same simplification i.e. composition independent fugacity coefficients.⁴¹ In connection to that, Heidemann and Michelsen⁵² have discussed that very strong negative deviations from ideality, which usually correspond to polymer mixtures or mixtures of strong electrolytes can potentially prevent the successive substitution approach from converging to the final stable solution.

A successive substitution approach, similar to the Rachford-Rice method can be also constructed, using Eqs. 35 - 37. Initially, Eq. 36 (also known as the Rachford-Rice equation) is solved with Newton's method for the phase fraction β at the current estimate of K -values and λ . Details and suggestions for an efficient implementation are given in Chapter 10 by Michelsen and Mollerup⁴¹. The values of the component mole fractions in each phase are again retrieved using Eqs. 49 - 50. Then, a new value for λ must be found and for this reason Eq. 37 is utilized. We have chosen to apply a successive substitution approach to update λ for the first 4 iterations and then convert to Newton's method for faster convergence. However, our numerical experiments have shown that in the first Newton iterations very large corrections may be obtained which can lead to divergence of the iterative procedure. Furthermore, the absolute value of λ usually spreads from 0 to 10 at the solution. Consequently, we have chosen to apply a damping factor to the Newton correction step, so that it always remains lower or equal to 1. The successive substitution update of λ is given by:

$$\lambda^{(k+1)} = \lambda^{(k)} + g(\lambda) \quad (51)$$

and the damped Newton's method is given by:

$$\lambda^{(k+1)} = \lambda^{(k)} + \delta\lambda^{(k)} \quad (52)$$

$$\delta\lambda^{(k)} = -D \cdot \left(\frac{dg(\lambda)}{d\lambda} \right)^{-1} g(\lambda) \quad (53)$$

with

$$g(\lambda) = \sum_{l=1}^{N_c} q_l w_l \beta \quad (54)$$

$$\frac{dg(\lambda)}{d\lambda} = -\beta(1-\beta) \sum_{l=1}^{N_c} q_l^2 \frac{w_l x_l}{z_l} \quad (55)$$

In our approach, we have found that $D = 0.1$ works best as the initial damping factor in each iteration and its value is successively halved until $|\delta\lambda^{(k)}| \leq 1$. The fugacity coefficients are calculated from an EoS at the new composition and the K -values are then calculated by:

$$\ln K_i = \ln \hat{\phi}_i^b(T, P, \mathbf{x}) - \ln \hat{\phi}_i^a(T, P, \mathbf{w}) - \lambda q_i; \quad i = 1, 2 \dots N_C \quad (56)$$

The procedure is repeated until convergence.

4. The Mean Ionic Approach in Phase Equilibrium Calculations

4.1. Single Electrolyte

Constructing an isothermal flash calculation method, based on the MIA, when only one electrolyte is present in a mixture of multiple solvents is relatively straightforward. However, as we have already discussed in the Introduction, particular attention must be paid to the material balance, since it must be formulated based on the true ionic composition of the mixture (molecular components and ionic species). Because of the existence of a single electrolyte $C_{v+}A_{v-}$, Eqs. 8 and 9 can be applied and the system of equations is simplified. If N_{Ions} is the number of ionic components in the mixture ($N_{Ions} = 2$ in this case), the $N_C + 1$ system of equations for a full Newton's method can be written:

$$g_i = \ln K_i + \ln \hat{\phi}_i^a(T, P, \mathbf{w}) - \ln \hat{\phi}_i^b(T, P, \mathbf{x}) = 0; \quad i = 1, 2 \dots (N_C - N_{Ions}) \quad (57)$$

$$g_+ = \ln K_+ + \ln \hat{\phi}_{\pm}^a(T, P, \mathbf{w}) - \ln \hat{\phi}_{\pm}^b(T, P, \mathbf{x}) = 0 \quad (58)$$

$$g_- = \ln K_- + \ln \hat{\phi}_{\pm}^a(T, P, \mathbf{w}) - \ln \hat{\phi}_{\pm}^b(T, P, \mathbf{x}) = 0 \quad (59)$$

Eqs. 57 - 59 are complemented with Eq. 36 as the $N_C + 1$ equation of the non-linear system. The vector of independent variables is $\mathbf{X} = (\ln K_1, \dots, \ln K_{N_C}, \beta)$. The elements of the Jacobian matrix for this equation set are readily retrieved from Eqs. 38, 39, 41 and 42. Eq. 58 or Eq. 59 can be replaced with the following equation as well:

$$g_{N_C} = \ln K_+ - \ln K_- = 0 \quad (60)$$

which is Eq. 8 expressed in logarithmic form. The mean ionic fugacity coefficients are calculated from Eq. 3. For the calculation of some Jacobian elements, the composition derivatives of the mean ionic fugacity coefficients are required. For phase 1 with composition \mathbf{w} , these are given by:

$$\frac{\partial \ln \hat{\varphi}_{\pm}^a(T, P, \mathbf{w})}{\partial w_j} = \frac{1}{v} \left(v_+ \frac{\partial \ln \hat{\varphi}_+^a(T, P, \mathbf{w})}{\partial w_j} + v_- \frac{\partial \ln \hat{\varphi}_-^a(T, P, \mathbf{w})}{\partial w_j} \right) \quad (61)$$

The Newton iteration is again expressed with Eqs. 47 and 48 and the new ionic composition is calculated after every iteration from Eqs. 49 and 50. The new composition is used in turn to calculate new fugacity coefficients from the thermodynamic model and the procedure is repeated until convergence.

Taking into account the discussion above, the Rachford-Rice method can be easily adjusted for systems of multiple solvents and one electrolyte. Similarly to the newly proposed first-order method that was presented in the previous Section, Eq. 54 is solved with Newton's method for the phase fraction β at the current estimate of K -values and subsequently, the values of the component mole fractions in each phase are retrieved using Eqs. 49 - 50. The fugacity coefficients are calculated from an EoS at the new composition and the new K -values are then calculated by:

$$\ln K_i = \ln \hat{\varphi}_i^b(T, P, \mathbf{x}) - \ln \hat{\varphi}_i^a(T, P, \mathbf{w}); \quad i = 1, 2 \dots (N_C - N_{Ions}) \quad (62)$$

$$\ln K_+ = \ln \hat{\varphi}_{\pm}^b(T, P, \mathbf{x}) - \ln \hat{\varphi}_{\pm}^a(T, P, \mathbf{w}) \quad (63)$$

$$\ln K_- = \ln \hat{\varphi}_{\pm}^b(T, P, \mathbf{x}) - \ln \hat{\varphi}_{\pm}^a(T, P, \mathbf{w}) \quad (64)$$

4.2. Multiple Electrolytes

As it has already been discussed in the Introduction, the formal extension of the MIA to mixtures of multiple electrolytes is complicated by the fact that the mean fugacity coefficients are not independent of each other. To elaborate more, we refer to our previous example of a mixture of two solvents that also contains Na^+ , Cl^- , K^+ and Br^- . We start from Eq. 6 (equilibrium relation expressed for each possible neutral cation-anion combination) and reformulate it as follows:

$$\sqrt[v]{w_+^{v_+} w_-^{v_-} \hat{\varphi}_{\pm}^a} = \sqrt[v]{x_+^{v_+} x_-^{v_-} \hat{\varphi}_{\pm}^b} \quad (65)$$

$$\sqrt[v]{\left(\frac{w_+}{x_+}\right)^{v_+} \left(\frac{w_-}{x_-}\right)^{v_-}} = \frac{\hat{\varphi}_{\pm}^b}{\hat{\varphi}_{\pm}^a} \quad (66)$$

$$\sqrt[v]{K_+^{v+} K_-^{v-}} = \frac{\hat{\phi}_\pm^b}{\hat{\phi}_\pm^a} \quad (67)$$

In our example, four possible salts can be formed e.g. NaCl, NaBr, KCl and KBr. Eq. 67 expresses the equilibrium relation for each possible salt and because the salts share common ions, not all equilibrium relations are independent. To correctly formulate an isothermal flash method, a linearly independent combination of electrolytes must be selected. This is equivalent to selecting a linearly independent set of dissociation reactions. To test for linear independence, we propose the construction of a stoichiometric matrix of the electrolyte system called \mathbf{E} where rows denote the possible salts and columns denote the ionic species. The elements of the matrix are the stoichiometric coefficients of the ionic species in each corresponding salt. In this example, the matrix takes the form:

$$\mathbf{E} = \begin{array}{c} \begin{array}{c} NaCl \\ NaBr \\ KCl \\ KBr \end{array} \begin{array}{c} Na^+ \\ Cl^- \\ K^+ \\ Br^- \end{array} \begin{bmatrix} 1 & 1 & 0 & 0 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 \end{bmatrix} \end{array} \quad (68)$$

In this case, $\text{rank}(\mathbf{E}) = 3$, which means that matrix \mathbf{E} is not full rank. Consequently, only 3 equilibrium relations are needed to describe this particular electrolyte system. Now, let's consider a mixture that contains 7 ionic species (Na^+ , Cl^- , K^+ , Br^- , Ca^{2+} , Li^+ and SO_4^{2-}) and form the stoichiometric matrix with all possible cation-anion combinations:

$$\mathbf{E} = \begin{array}{c} \begin{array}{c} NaCl \\ NaBr \\ Na_2SO_4 \\ KCl \\ KBr \\ K_2SO_4 \\ CaCl_2 \\ CaBr_2 \\ CaSO_4 \\ LiCl \\ LiBr \\ Li_2SO_4 \end{array} \begin{array}{c} Na^+ \\ Cl^- \\ K^+ \\ Br^- \\ Ca^{+2} \\ Li^+ \\ SO_4^{-2} \end{array} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 0 & 1 \\ 0 & 2 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 2 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2 & 1 \end{bmatrix} \end{array} \quad (69)$$

In this example, $\text{rank}(\mathbf{E}) = 6$. Again the matrix is not full rank. To generalize, $\text{rank}(\mathbf{E}) = N_{Ions} - 1$. Consequently, only $N_{Salts} = N_{Ions} - 1$ equilibrium relations, expressed for a

linearly independent combination of salts, are needed for the phase equilibrium calculation. Of course, the combination of salts is not unique, but the stoichiometric matrix is required to be full rank. In practice, this means that there should not be any column with all elements 0 or in other words, each ion must appear at least once in the matrix. For the above example, a correct stoichiometric matrix could be:

$$\mathbf{E} = \begin{matrix} NaCl \\ NaBr \\ Na_2SO_4 \\ KCl \\ CaCl_2 \\ LiCl \end{matrix} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \quad (70)$$

The matrix \mathbf{E} that appears in Eq. 70 is full rank ($\text{rank}(\mathbf{E}) = 6$), i.e. a linearly independent set of salts was chosen. As we discussed previously, the vector of independent variables for the two-phase isothermal flash is $\mathbf{X} = (\ln K_1, \dots, \ln K_{N_C}, \beta)$. Consequently, we need $N_C + 1$ equations to describe the problem, but we have $N_C - 1$ equilibrium relations, ($N_C - N_{Ions}$ for molecular components and $N_{Ions} - 1$ for the salts). The two additional equations are the material balance and the electro-neutrality condition. Eq. 67 can be reformulated with the use of the stoichiometric matrix \mathbf{E} and the equation set becomes:

$$g_i = \ln K_i + \ln \hat{\phi}_i^a(T, P, \mathbf{w}) - \ln \hat{\phi}_i^b(T, P, \mathbf{x}) = 0; \quad i = 1, 2 \dots (N_C - N_{Ions}) \quad (71)$$

$$g_k = \sum_{l=1}^{N_{Ions}} E(k, l) \left(\ln K_l + \ln \hat{\phi}_{k\pm}^a(T, P, \mathbf{w}) - \ln \hat{\phi}_{k\pm}^b(T, P, \mathbf{x}) \right) = 0; \quad k = N_C - N_{Ions} + 1 \dots N_C - 1 \quad (72)$$

$$g_{N_C} = \sum_{l=1}^{N_C} z_l \frac{K_l - 1}{1 - \beta + \beta K_l} = 0 \quad (73)$$

$$g_{N_C+1} = \sum_{l=1}^{N_C} q_l w_l = 0 \quad (74)$$

The mean ionic fugacity coefficients can be generalized with the help of the stoichiometric matrix:

$$\ln \hat{\phi}_{k\pm}^a(T, P, \mathbf{w}) = \frac{1}{\sum_{l=1}^{N_{Ions}} E(k, l)} \sum_{l=1}^{N_{Ions}} E(k, l) \ln \hat{\phi}_l^a(T, P, \mathbf{w}) \quad (75)$$

Eqs. 71 - 74 can be solved as a system of non-linear equations with Newton's method, as described in the previous sections.

A first-order method, similar to the Rachford-Rice approach can be also constructed. As in the previously developed methods, Eq. 73 is solved with Newton's method for the phase fraction β at the current estimate of K -values and subsequently, the values of the component mole fractions in each phase are retrieved using Eqs. 49 - 50. Then, the fugacity coefficients for each phase are reevaluated using the thermodynamic model available and the new K -values for the molecular components are calculated using Eq. 62. For the ionic species, however, a second system of equations must be solved. That is, Eqs. 72 and 74 expressed as:

$$g_k = \sum_{l=1}^{N_{Ions}} E(k, l) \left(\ln K_l + \ln \hat{\varphi}_{k\pm}^a(T, P, \mathbf{w}) - \ln \hat{\varphi}_{k\pm}^b(T, P, \mathbf{x}) \right) = 0; \quad k = 1 \dots N_{Salts} \quad (76)$$

$$g_{N_{Salts}+1} = \sum_{l=1}^{N_{Ions}} \frac{K_l z_l q_l}{1 - \beta + \beta K_l} = 0 \quad (77)$$

Eq. 77 is equivalent to Eq. 74, but with mole fractions replaced by the corresponding K -value expressions. This choice here is not essential, rather than serves a more uniform set of equations. Eqs. 76 and 77 are solved for $\mathbf{X} = (\ln K_1, \dots, \ln K_{N_{Ions}})$ with Newton's method, but for simplicity we choose to make the assumption of composition independent fugacity coefficients. The elements of the respective Jacobian are:

$$J_{k,l}^S = \frac{\partial g_k}{\partial \ln K_l} = E(k, l); \quad k = 1 \dots N_{Salts}, \quad l = 1 \dots N_{Ions} \quad (78)$$

$$J_{N_{Salts}+1,l}^S = \frac{\partial g_{N_{Salts}+1}}{\partial \ln K_l} = \frac{(1 - \beta) K_l z_l q_l}{(1 - \beta + \beta K_l)^2}; \quad l = 1 \dots N_{Ions} \quad (79)$$

In this way, all K -values (molecular components and ionic species) are updated and the procedure can be repeated until convergence.

5. Thermodynamic modelling with the eSAFT-VR Mie EoS

Thermodynamic modeling of electrolytes is a highly important and active research area. Currently two major categories of models exist, activity coefficient models that are the standard practice in the industry and electrolyte EoS that are the focus of recent research activity.⁵³ Successful activity coefficient models for electrolyte solutions include the Pitzer

model,⁵⁴ as well as local composition models like extended UNIQUAC⁵⁵ and the electrolyte NRTL⁵⁶. EoS for solutions containing ionic species are developed by accounting for both long- and short-range interactions within a solution. Long-range interactions account for ion – ion interactions and are described using a Debye–Hückel⁵⁷ or a Mean Spherical Approximation⁵⁸ term. In some EoS a Born⁵⁹ term is also added for the ion – solvent interactions. The terms for short-range interactions originate from traditional non-electrolyte EoS. Both types of models are summarized and discussed in the book by Kontogeorgis and Folas.^{60–62}

The newly introduced methodology for the calculation of phase equilibrium requires fugacity coefficients that in this work are provided by a relatively new SAFT variant, the eSAFT-VR Mie EoS.⁶³ The non-electrolytic SAFT-VR Mie EoS^{64–66} has been extended to electrolyte solutions by adding a DH⁵⁷ and a Born⁵⁹ term and has been used for aqueous mean ionic activity coefficients, osmotic coefficients, liquid density, vapor pressure and hydration energies⁶³ as well as gas solubility in aqueous electrolyte solutions.²⁹ In the work of Novak et al.²⁹ addressing gas solubility in aqueous electrolyte solutions, the ions are artificially restricted to the liquid phase by setting their vapor fraction to zero ($y_{Ion} = 0$), similarly to the work of Held et al. with ePC-SAFT.³⁰

To showcase the differences between the new methodology and the MIA in phase equilibrium calculations, we have applied the approach to the phase equilibrium of three different systems, methanol – water – KCl (VLE), benzene – water – NaCl (LLE) and 1-propanol – water – NaCl (LLE). These systems were selected as representatives of the possible applications of phase equilibrium of electrolyte solutions. In this first part of this section the performance of our model in mixed solvent VLE and LLE is tested.

The pure component parameters of SAFT-VR Mie for molecular components used in this work are tabulated in Table 1. For 1-propanol no pure component parameters from the literature can be used, as this component has been previously modelled with a SAFT-VR Mie variant with a different association term.⁶⁷ Our version of the model incorporates the association term as introduced by Dufal et al.⁶⁵ and the pure component parameters for 1-propanol were fitted in this work based on liquid density and vapor pressure of DIPPR correlations in the temperature range of 270 – 510 K. The parameters of ions and ion – water interactions are all taken from our previous works and are tabulated in Table 2. The relative permittivity of a pure liquid solvent, ϵ_r^{pure} , within eSAFT-VR Mie is determined according to the correlations shown in Table 3. For benzene no such correlation existed and thus it is determined in this work (Figure 1).

Extension of SAFT-VR Mie to mixtures is achieved through mixing and combining rules presented in the original publications of the model.⁶⁴⁻⁶⁶ The combining rules that are relevant in this work are shown in the following equations, between components i and j :

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \frac{\sqrt{\sigma_{ii}^3\sigma_{jj}^3}}{\sigma_{ij}^3} (1 - k_{ij}) \quad (80)$$

$$\varepsilon_{abij}^{HB} = \sqrt{\varepsilon_{abii}^{HB}\varepsilon_{abjj}^{HB}} \quad (81)$$

$$K_{abij} = \left(\frac{\sqrt[3]{K_{abii}} + \sqrt[3]{K_{abjj}}}{2} \right)^3 \quad (82)$$

where ε_{ij} is the unlike dispersion energy between molecules i and j , σ_{ii} is the segment diameter of component i , ε_{ii} is the dispersion energy of molecule i , k_{ij} is a binary interaction parameter, ε_{abij}^{HB} is the cross-association energy and K_{abij} the cross-association bonding volume of components i and j and finally, ε_{abii}^{HB} is the self-association energy and K_{abii} the bonding volume of component i .

In this work, the unlike association parameters, ε_{abij}^{HB} and K_{abij} , are non-zero between all molecular species. For methanol – water and 1-propanol – water mixtures, the cross-association parameters are determined through Eqs. 81 and 82, while for benzene – water mixtures, where benzene is solvating in water, the cross-association energy is 0.6 - the value of pure water - and the cross-association volume equal to that of pure water, as suggested by Novak et al.⁶⁸

SAFT-VR Mie has been optimized in modelling the binary mixtures of the non-ionic species by adjusting a binary interaction parameter, k_{ij} . The values of the binary interaction parameters used in this work are reported in Table 4. For the binary methanol – water mixture an interaction parameter was fitted based on the liquid phase compositions and the correlation of the model in VLE calculation at atmospheric pressure was deemed satisfactory (Figure 2). For benzene – water at atmospheric pressure and room temperature the solubility of benzene in water was significantly underestimated, consistent with the inability of the model to capture the solubility minimum.⁶⁸ For this reason, a binary interaction parameter was introduced to fit this property. Similarly, for 1-propanol – water mixture the interaction parameter value was fitted to reproduce the VLE data at atmospheric pressure. However, this resulted in a false prediction of an LLE split at lower temperatures, as shown in Figure 3. This LLE split is indeed a characteristic of longer chain n-alcohols with water, starting from 1-butanol.

Dispersion energy between ions and water is a fitted parameter for eSAFT-VR Mie model, and its values are temperature dependent, as shown in Table 2. For the ion – ion dispersion interactions eSAFT-VR Mie utilizes Eq. 83, that is essentially the Hudson and McCoubrey⁶⁹ combining rules, as formulated by Haslam et al.⁷⁰ for Mie fluids:

$$\varepsilon_{ij} = \frac{3}{8} \frac{a_{0,i} a_{0,j}}{(4\pi\varepsilon_0)^2 \sigma_{ij}^6} \frac{I_i I_j}{I_i + I_j} \quad (83)$$

where ε_{ij} is the dispersion energy between ions, $a_{0,i}$ is the electronic polarizability of ion i , I_i the ionization potential and σ_{ij} the unlike segment diameter. The same approach is also adopted in this work for the dispersion energy between ions and the second molecular component besides water, shown in Eq. 84:

$$\varepsilon_{ij} = 2 \frac{\sqrt{C_{ii} C_{jj}} \sigma_{ii}^3 \sigma_{jj}^3}{C_{ij}} \frac{\sqrt{I_i I_j}}{\sigma_{ij}^6 (I_i + I_j)} \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad (84)$$

where C_{ij} is the pre-factor for the Mie potential.

In this work, we have applied the methodology for methanol, benzene and 1-propanol with ions, using the ionization energy values: $I_{methanol} = 10.85 \text{ eV}$, $I_{benzene} = 9.24 \text{ eV}$ and $I_{1-propanol} = 10.22 \text{ eV}$.⁷¹ Although Novak et al.²⁹ showed that this approach for gas solubility in aqueous electrolytes may result in large deviations from experimental data, it is the only available predictive methodology. For this reason it was used here, since the focus of this work is the validation of the newly proposed methodology for phase equilibrium calculations, and not the eSAFT-VR Mie optimization for such calculations. An extensive evaluation of mixed solvent electrolyte solutions in VLE and LLE as well as the model optimization via fitting will be part of future work.

For mixed solvents, a mixing rule is also needed to calculate the dielectric constant of the mixture. The available options proposed in the literature are usually linear mixing rules based on mole fraction,⁷² weight fraction²³ or volume fraction⁷³. Actually the volume fraction based mixing rule has been introduced for the polarizability^{74,75} or for the coefficients of the various correlations,⁷⁶ but in our study we chose to use it directly for the dielectric constant (Eq. 85). In this work all systems are studied at conditions where all the molecular components are condensable and therefore the liquid molar volume is estimated by SAFT-VR Mie EoS. At conditions where one of the solvents is not in the liquid state, the modification of Wang and Anderko⁷⁵ can be used instead.

$$\varepsilon_r^{mix} = \frac{\sum_{i=1}^{solvents} x_i v_i \varepsilon_r^{pure,i}}{\sum_{i=1}^{solvents} x_i v_i} \quad (85)$$

where x_i is the mole fraction of component i , v_i is the liquid molar volume of component i and $\varepsilon_r^{pure,i}$ is the relative permittivity of pure component i . Since more than one mixing rules

have been proposed, we decided to test which one performed better for mixtures of polar – polar and polar – non-polar components. A comparison of three different options showed that the volume fraction based mixing rule (Eq. 85) was the only one that performed consistently well for all types of mixtures (Figure 4) and for this reason it is used in the rest of this work.

VLE of mixed solvents has been addressed in the literature and most models are able to capture the effect of salting out rather accurately.^{27,76–79} In this work, we will be discussing the ternary system methanol – water – KCl, in an entirely predictive approach, since the focus of this paper is the derivation and validation of the new calculation methodology and not the optimization of the model. As shown in Figure 2, the predictions for both the binary and ternary system are satisfactory, regardless of the predictive approach. As it is typically done in the literature for VLE calculations, we have calculated the phase equilibrium by enforcing the ionic composition in the vapor phase to zero.

LLE calculations of water with liquid hydrocarbons in the presence of salts are not typically presented in the literature, possibly due to the lack of experimental data. Predictions with SAFT-VRE are presented by Patel et al.³³ that show a salting out effect of alkanes from water when salt is introduced, but unfortunately no experimental verification is possible. Some experimental data for solubility of cyclohexane and benzene in aqueous electrolytes exist in the literature, discussed by Wang and Anderko²⁴ using their excess Gibbs energy model. The authors have used ternary data (water – hydrocarbon – salt) to fit hydrocarbon – ion interactions, and by doing so they are able to accurately reproduce the hydrocarbon solubility. The predictions of eSAFT-VR Mie for the same system are shown in Figure 5; they are in qualitative agreement with experimental data. Quantitative agreement can be achieved if the benzene – ion interactions are fitted to the ternary experimental data. These results have been generated using the MIA.

Last but not least, the LLE of 1-propanol – water – NaCl is addressed. In the literature there are very few modelling results for LLE of alcohol – water – salts. To our knowledge there are very few publications showing EoS modeling of this specific system, such as by Maribo-Mogensen et al.⁸⁰ and the thesis of M. Bülow⁸¹ with eCPA with varying success and the work of Zuo and Zhang²¹ with their electrolyte EoS and eNRTL. The predictions of eSAFT-VR Mie are shown in Figure 6. The model predicts a wider composition range where phase split occurs compared to the experimental data. There are more results with 1-butanol – water – salt modeling, but again the accuracy of the models varies significantly.^{21,27,37,40,77,81}

6. Application of the new methodology and comparison with the Mean

Ionic Approach

The different methodologies presented in this work are the mean ionic Rachford-Rice approach (MIA RR), the mean ionic second order (MIA 2nd), and the EIA methodology formulated as a first order method (EIA RR) or second order (EIA 2nd). They all yield identical phase equilibrium compositions in the three systems presented earlier, VLE of methanol – water – KCl, LLE of benzene – water – NaCl and LLE of 1-propanol – water – NaCl. In this paragraph the different methodologies are compared in terms of robustness and convergence rate by employing the error calculated as:

$$error^i = \ln \sqrt{(\beta^i - \beta^\infty)^2 + (\lambda^i - \lambda^\infty)^2 + \sum_J^{NC} (K_j^i - K_j^\infty)^2} \quad (86)$$

where the superscripts denote the value of the variable at the iteration i and at the solution ∞ .

For all the different approaches, the compositions of the molecular components are initialized using the salt-free system at the same temperature and pressure. For this purpose, a PT flash calculation is performed for the molecular components. The resulting mole fractions of the two phases are used as the composition initialization for the molecular components in the electrolyte solution. Regarding the initial composition of the ions in the liquid phases, it is determined by assuming that the molality of all phases is the same and equal to that of the feed phase. For the vapor phases, where a very low ionic concentration is expected, the ionic composition is initialized with arbitrary, very small ion mole fractions of 10^{-10} . Last but not least, the convergence criterion used in this work is $\|g\|_2 \leq 10^{-8}$.

The performance of the different methodologies in terms of convergence rate in single salts is compared for methanol – water – KCl VLE in Figure 7, benzene – water – NaCl in Figure 8 and 1-propanol – water – NaCl LLE in Figure 9 respectively. From these figures it is clear that the first order methods require approximately double the number of iterations than the second order ones to achieve convergence and that the two second order methods -the EIA and MIA- show identical behavior for single salts.

As explained earlier, ions are known not to migrate to the vapor phase. Thus, the standard approach in the literature for VLE calculations is enforcing the ionic composition in the vapor phase equal to zero. For methanol – water – KCl VLE this method is shown as well, denoted as RR enforce $y = 0$ in Figure 7. The newly proposed methods are applied with the ions being free to distribute between both phases. However, in the vapor phase, an arbitrary,

low value of relative permittivity ($\epsilon_r^{vapor} = 3$) is assigned, so that ions are driven away from this phase. An alternative to this is using a density dependent relative permittivity as discussed earlier. The reason for allowing the ions to distribute according to the thermodynamic model, and not enforce their composition, apart from the thermodynamic consistency, is the convenience and flexibility of having a unified framework for phase equilibrium calculations, either VLE or LLE. In the case of the methanol – water – KCl VLE, the equilibrium compositions of the vapor phase determined by artificially restricting the ions to the liquid phase is naturally zero. On the other hand, when a very low dielectric constant for the vapor phase is used and the ions are allowed to distribute in both phases, the equilibrium vapor ionic composition is found lower than 10^{-15} . The rest of the results are practically identical between the two methods, shown in Figure 2.

The sensitivity of the second-order methodologies to the initial estimates was also verified with our numerical experiments. This is a general characteristic of second order methods for molecular components as well and it is usually addressed with a few steps of successive substitution updates in the first iterations. To improve the robustness of the proposed methodology we propose some of the initial iterations (3 – 8) to be performed in a partial Newton, composition independent scheme. This is achieved by using the same equation set as the second order method, but setting the composition derivatives of the fugacity coefficients with mole numbers equal to zero. After these few iterations, the calculation methods are switched to full Newton schemes, taking into account the compositional derivatives as well.

Using zero compositional derivatives of the fugacity coefficients with mole numbers in second order schemes is directly equivalent to the first order methods and produces the same convergence rate as the successive substitution approach, as both are based on the same simplification. This is shown in Figures 7 - 9, where for the first 3 – 8 iterations, depending on the system, the convergence rate of the 2nd order MIA and EIA methods is identical to the MIA-RR. The reason that the EIA 2nd order reduces to the MIA-RR and not the EIA-RR method is the successive substitution scheme used for λ (Eqs. 51 - 55). For this reason, it is preferred to use the EIA 2nd order method with zero compositional derivatives to using the EIA-RR method. Furthermore, this approach is very important for models where compositional derivatives are not available; they can be omitted at the cost of a slower convergence rate.

There is also another reason why the EIA-RR scheme converges in more iterations than the MIA-RR. For the first 4 iterations, a successive substitution approach to update λ is

proposed. Afterwards, a Newton's method is used for faster convergence. However, it was found that for some Newton iterations, usually the first ones, the calculated Newton step was too large, which led to divergence of the iterative procedure. To enhance the robustness of the method, we have chosen to apply a damping factor to the Newton correction step, so that it always remains lower or equal to 1. In our approach, $D = 0.1$ initially in each iteration and its value is successively halved until $|\delta\lambda^{(k)}| \leq 1$. This decision was based on the need for robustness being greater than that of higher convergence rate. However, the EIA 2nd order method with zero compositional derivatives, which is equivalent to a first order method does not possess the undesirable characteristics of the EIA-RR and should be preferred.

For multiple salts, three test systems are introduced, the first two being 1-propanol – water – NaCl – KBr and 1-propanol – water – NaCl – KCl. In Figure 10 the K -values at LLE calculated with the different methodologies are presented. Our newly introduced ionic methodology treats the first system as 1-propanol – water – Na^+ – Cl^- – K^+ – Br^- , while the MIA utilizes three salts, NaCl, NaBr, KBr (as proven earlier the number of linearly independent salts is the $N_{Ions} - 1$). The second system is treated as 1-propanol – water – Na^+ – Cl^- – K^+ with the EIA and NaCl, KCl with the MIA. It is shown that if the procedure discussed in Section 4.2 is followed, the MIA yields identical results with the EIA methodology. However, the EIA methodology is by far less complex to implement and readily extendable to more ions, which is its main advantage.

To further showcase this complexity, another test system with seven ions is presented: 1-propanol – water – Na^+ – Cl^- – K^+ – Br^- – Ca^{2+} – Li^+ – SO_4^{2-} , shown in Figure 11. Before discussing about the different methodologies it is important to notice the equilibrium compositions that were calculated, shown in Table 5. 1-propanol is salted out almost entirely by the presence of ions. Furthermore, most ions have very strong preference for the water phase compared to the alcohol phase. K^+ is the only cation that shows some affinity to 1-propanol, while the anions distribute more evenly in the two phases, apart from SO_4^{2-} . If one compares the K -values of the ions with their dispersion energy parameter with water ($\epsilon_{\text{ion,water}}$) a correlation is found. The ions that have the smaller values of $\epsilon_{\text{ion,water}}$ are the ones that have the higher K -values therefore they can also be found in the alcohol phase. K^+ has the smallest value between the selected cations, and Cl^- with Br^- the smallest values between anions, with a very small difference between them. Therefore both can be found in the alcohol phase. It would be of great interest to compare these observations with experimental data. Unfortunately, such experimental data to the best of our knowledge do not exist.

To return to the comparison of the different methodologies, our ionic methodology requires only the charges of the ions. The MIA on the other hand additionally requires the stoichiometric coefficient matrix of the linearly independent salts. One of the possible stoichiometric matrices is shown in Eq. 79, where the selected salts are $NaCl$, $NaBr$, Na_2SO_4 , KCl , $CaCl_2$ and $LiCl$. Naturally, the equilibrium compositions between the two methods are the same; however the introduction of the stoichiometric coefficient matrix is not easy to generalize. Furthermore, as is shown in Figure 11, the EIA 2nd order approach with zero compositional derivatives requires the same number of iterations for convergence as the MIA RR. To conclude, the EIA approach is equivalent in terms of convergence rate, but far less complex to implement for multiple salts, and for this reason it should be preferred.

7. Conclusions

This work describes in detail the current status of physical phase equilibrium calculation methods for fully dissociating electrolyte solutions at constant temperature, pressure and feed phase composition (PT flash) and introduces a new way to derive and solve the corresponding phase equilibrium relations. The model used in this work for the calculation of thermodynamic properties is the eSAFT-VR Mie EoS and is treated as a predictive tool.

The new framework for phase equilibrium calculations, the Electrochemical Ionic Approach (EIA), is rigorously derived by treating phase equilibrium as a minimization problem of the Gibbs free energy and utilizing the electro-neutrality condition as a constraint. The constraint is used to formulate a Lagrange function, which serves as the basis to derive the equations that govern the phase equilibrium problem. The Lagrange multiplier which corresponds to the electro-neutrality constraint is shown to have a theoretical meaning, being proportional to the difference in the electrostatic potential between the phases at equilibrium. Two numerical methods for solving the new phase equilibrium framework are presented, a first order, successive substitution approach similar to the classic Rachford-Rice method and a second-order one, which is a full Newton's method.

Furthermore, the most popular approach in the literature, the Mean Ionic Approach (MIA), is also mathematically formulated as an isothermal flash calculation in first and second-order schemes for single salts. Both schemes produce identical results with the new methodology. However, in terms of performance, the EIA formulated as a second-order

scheme and coupled with a few initial steps of composition independent fugacity coefficients is the most attractive option and is thus proposed for implementation.

Last but not least both methodologies were applied to phase equilibrium calculations of multiple salts as well. An extension of the MIA to multiple salts was formulated and presented in detail. It was shown that it is a non-trivial task to correctly apply the MIA in multiple salt solutions, as a linearly independent set of salts has to be determined a priori. A detailed analysis and mathematical justification to perform this selection was formally presented in this work. Due to the need to establish a set of linearly independent salts, the MIA is not easy to generalize for multiple salt solutions and becomes increasingly more complicated as the number of ions in the solution increases. On the other hand, the EIA is directly applicable to multi-salt solutions due to its ionic nature, and is therefore recommended.

Future work will be directed toward the generalization of the new methodologies to three phase equilibria (VLLLE), as well as the development of stability analysis and phase diagram calculation methods.

Acknowledgements

The authors are thankful the European Research Council (ERC) for funding this research under the European Union's Horizon 2020 research and innovation program (grant agreement No 832460), ERC Advanced Grant project "New Paradigm in Electrolyte Thermodynamics". The authors wish to thank Professor Kaj Thomsen and Dr. Bjorn Maribo-Mogensen for the stimulating discussions and important suggestions.

Credit authorship contribution statement

Ilias K. Nikolaidis: Methodology, Software, Validation, Formal analysis, Investigation, Writing - original draft, Visualization, Data curation. **Nefeli Novak:** Methodology, Software, Validation, Formal analysis, Investigation, Writing - original draft, Visualization, Data curation. **Georgios M. Kontogeorgis:** Writing - review & editing, Project administration, Funding acquisition. **Ioannis G. Economou:** Resources, Writing - review & editing, Supervision, Project administration

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Georgios Kontogeorgis reports financial support was provided by European Research Council.

Nomenclature

C	Prefactor of eSAFT-VR Mie EoS
D	Dumping factor
e	Elementary charge
$error^i$	Error in iteration i
E	Stoichiometric matrix
\hat{f}	Fugacity
\mathcal{F}	Faraday's constant
\mathbf{g}	System of equations describing phase equilibrium
G	Gibbs free energy
J	Jacobian matrix
k_{ij}	Binary interaction parameter
K	K-values
m	Mean molality apart from Table 1. In table 1, m is the segment number in eSAFT-VR Mie
ns	Mole numbers in the apparent fugacity approach
\hat{n}_i	Mole number of component i
N_C	Number of components
N_P	Number of phases
P	Pressure
\mathbf{q}	Electrovalency vector
R	Gas constant
T	Temperature
U	Internal energy
\tilde{U}	Internal energy with the electrochemical contribution
U^e	Electrochemical contribution of the internal energy
v	Liquid molar volume
\mathbf{w}	Mole fraction vector of the second liquid phase in LLE
\mathbf{X}	Unknown variables in the system of equations describing phase equilibrium
x_i^a	Mole fraction of component i in phase a
\mathbf{x}	Mole fraction vector of the liquid phase
\mathbf{y}	Mole fraction vector of the vapor phase
\mathbf{z}	Mole fraction vector of the feed phase

Greek and other symbols

a_0	Electronic polarizability
β	Phase fraction
γ	Mean ionic activity coefficient
γ_{\pm}^m	Mean ionic activity coefficient on a molality scale
γ_{\pm}^*	Asymmetric mean ionic activity coefficient on a mole fraction scale
ε	Dispersion energy
ε_{ab}^{HB}	Cross-association energy between sites a and b
ε_r	Relative permittivity
I	Ionization potential
K_{ab}	Cross-association bonding volume
λ_a	Lagrange multiplier
$\lambda = \frac{\lambda_a}{RT}$	Lagrange multiplier over RT
μ	Chemical potential without the electrochemical contribution
$\tilde{\mu}$	Chemical potential with the electrochemical contribution or electrochemical potential
v_{ij}	Stoichiometric coefficient of ion i in salt j . If j is omitted only one salt is considered
v	Sum of stoichiometric coefficients for all ions in a salt
σ	Segment diameter
$\hat{\phi}$	Fugacity coefficient without the electrostatic potential contribution
$\tilde{\phi}$	Fugacity coefficient with the electrostatic potential contribution
ψ	Electrostatic potential
\mathcal{L}	Lagrange function

Subscripts and Superscripts

\pm	Mean value of property
app	Apparent value of property
i, j, k, l	Component index or iteration number
o	Reference value
a, b	Phase index
+	Cation
-	Anion
S	Salt
mix	Mixture
∞	Value at the solution

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Tables

Table 1. Pure component parameters of SAFT-VR Mie used in this work.

Component	m	σ (Å)	λ_r	ε/k_B (K)	$\varepsilon_{ab}^{HB}/k_B$ (K)	K_{ab}^{HB} (Å ³)	Association scheme
Water ⁶⁵	1	3.0555	35.823	418	1600	496.66	4C
Methanol ⁶⁵	1.7989	3.1425	16.968	276.92	2156.00	222.18	3B
1-Propanol ^a	1.8902	3.8562	14.5167	314.97	2734.27	79.39	2B
Benzene ⁶⁶	2.2785	3.7806	11.594	297.53	-	-	Solvating with water

^a: Determined in this study by fitting vapor pressure (AARD=0.3%) and liquid density (AARD=0.3%) in the

range 270-510 K. $AARD\% = \frac{100}{NP} \sum_1^{NP} \left(\left| \frac{prop^{exp} - prop^{calc}}{prop^{exp}} \right| \right)$.

Table 2. Ionic parameters of eSAFT-VR Mie from the literature used in this work.^a

Ion	$\varepsilon_{0,water,ion}/k_B$ (K) ^b	$\varepsilon_{1,water,ion}$ (K) ^b	σ (Å) ⁶³	a_{Born} (Å) ^{63,82}	I (eV)	a_0 (10 ⁻²⁴ cm ³)
Na ⁺	1620.70	263.62	2.1607	3.360	47.286	0.179
K ⁺	1134.90	280.18	2.6273	4.344	31.630	0.830
Cl ⁻	420.46	-123.09	3.0999	3.874	3.613	3.660
Br ⁻	462.24	-52.43	3.4887	4.174	3.364	4.770

^a: Ions are non-associating species with $\lambda_a = 6$, $\lambda_r = 12$ and $m = 1$.

^b: Dispersion energy parameters enter into $\frac{\varepsilon_{water,ion}}{k_B} = \frac{\varepsilon_{0,water,ion}}{k_B} \left(1 - \frac{\varepsilon_{1,water,ion}}{T} \right)$ by Novak et al.²⁹

Table 3. Correlations for the dielectric constant of pure components (ε_r^{pure}) with temperature (T in K).

Component	ε_r^{pure}
Water ⁸³	$-19.2905 + \frac{29814.5}{T} - 0.0196789 T + 0.013189 \cdot 10^{-2} T^2 - 0.031144 \cdot 10^{-5} T^3$
Methanol ⁸³	$10^{1.514 - 0.00264(T - 298.15)}$
1-Propanol ⁸³	$173.19 - \frac{151.07}{T} - 0.36873 T - 0.19387 \cdot 10^{-2} T^2 + 0.49023 \cdot 10^{-5} T^3$
Benzene ^a	$1.409 + \frac{255.99}{T}$

^a: Determined in this study (see Figure 1).

Table 4. Binary interaction parameters, k_{ij} , between molecular components used in SAFT-VR Mie.

Binary	k_{ij}	Optimized property
Methanol – Water	0.015	VLE at 0.1 MPa
1-Propanol – Water	-0.08	VLE at 0.1 MPa
Benzene – Water	-0.024	Benzene solubility at 0.1 MPa and 298.15 K

Table 5. LLE equilibrium results for the system water - 1-propanol - 7 ions, at 298.15 K and 0.1 MPa.

	Mole fraction in feed phase	Mole fraction in aqueous phase	Mole fraction in alcohol phase
Water	0.546	0.749	0.139
1-propanol	0.285	1.59E-05	0.859
Na ⁺	0.0211	0.0315	1.40E-06
Cl ⁻	0.0421	0.0628	5.04E-04
K ⁺	0.0211	0.0310	1.11E-03
Br ⁻	0.0211	0.0312	6.10E-04
Ca ²⁺	0.0211	0.0315	6.55E-19
Li ⁺	0.0211	0.0315	2.50E-11
SO ₄ ²⁻	0.0211	0.0315	3.87E-08

Figures

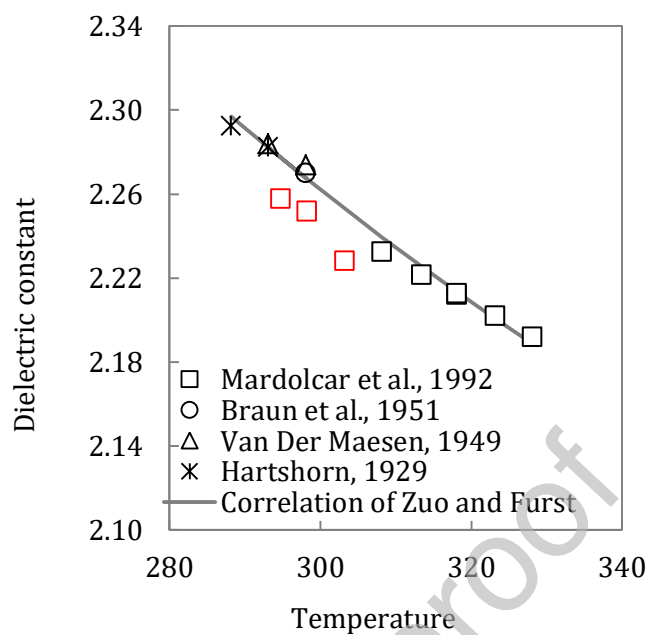


Figure 1. Dielectric constant of liquid benzene at atmospheric pressure. Points are experimental data,⁸⁴⁻⁸⁶ line corresponds to a correlation fitted in this work (see Table 3). Red points have been excluded from the correlation as outliers.

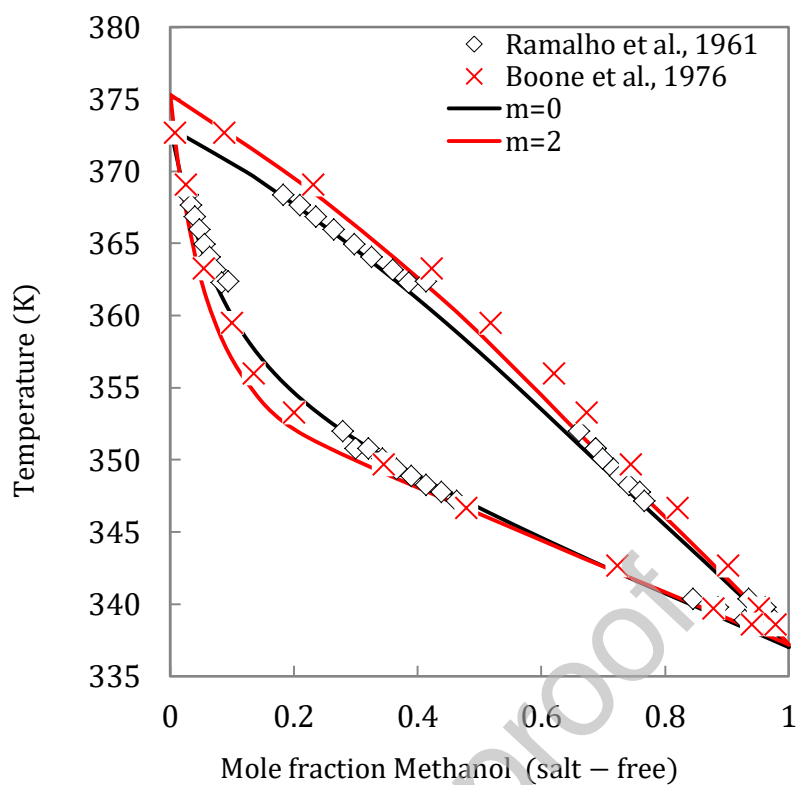


Figure 2. VLE of methanol - water - KCl at atmospheric pressure. Points correspond to experimental data,^{87,88} lines to eSAFT-VR Mie predictions. Experimental data and calculations for the methanol - water binary mixture are shown in black and for Methanol - Water - KCl ternary mixture at salt molality 2 mol/kg water in red.

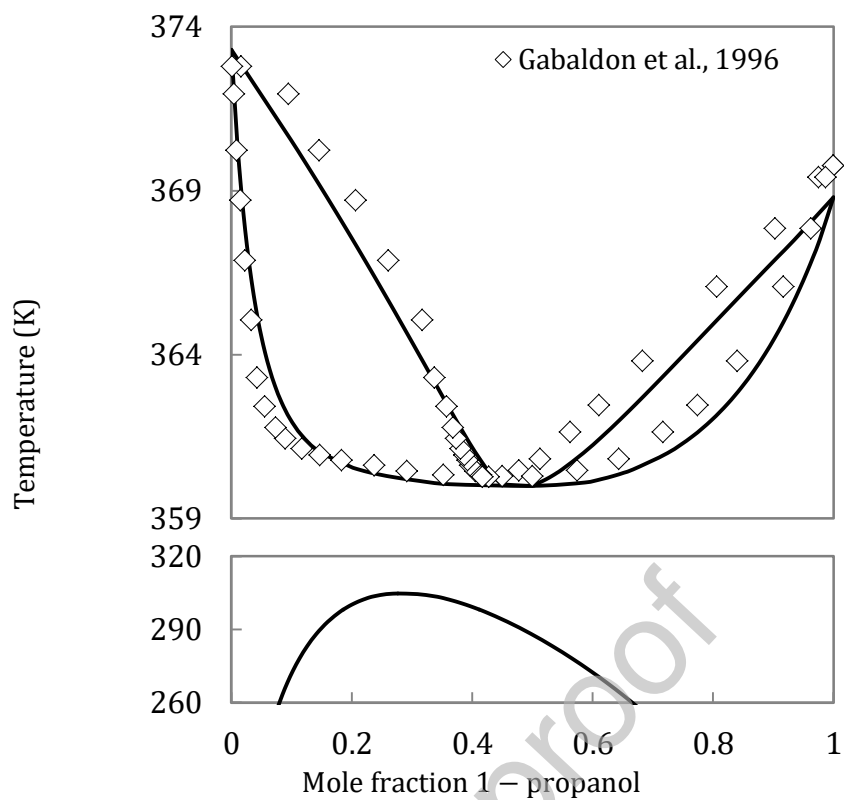


Figure 3. Phase diagram of 1-propanol - water with SAFT-VR Mie. Points are experimental data,⁸⁹ lines are SAFT-VR Mie predictions using the binary interaction parameter of Table 4.

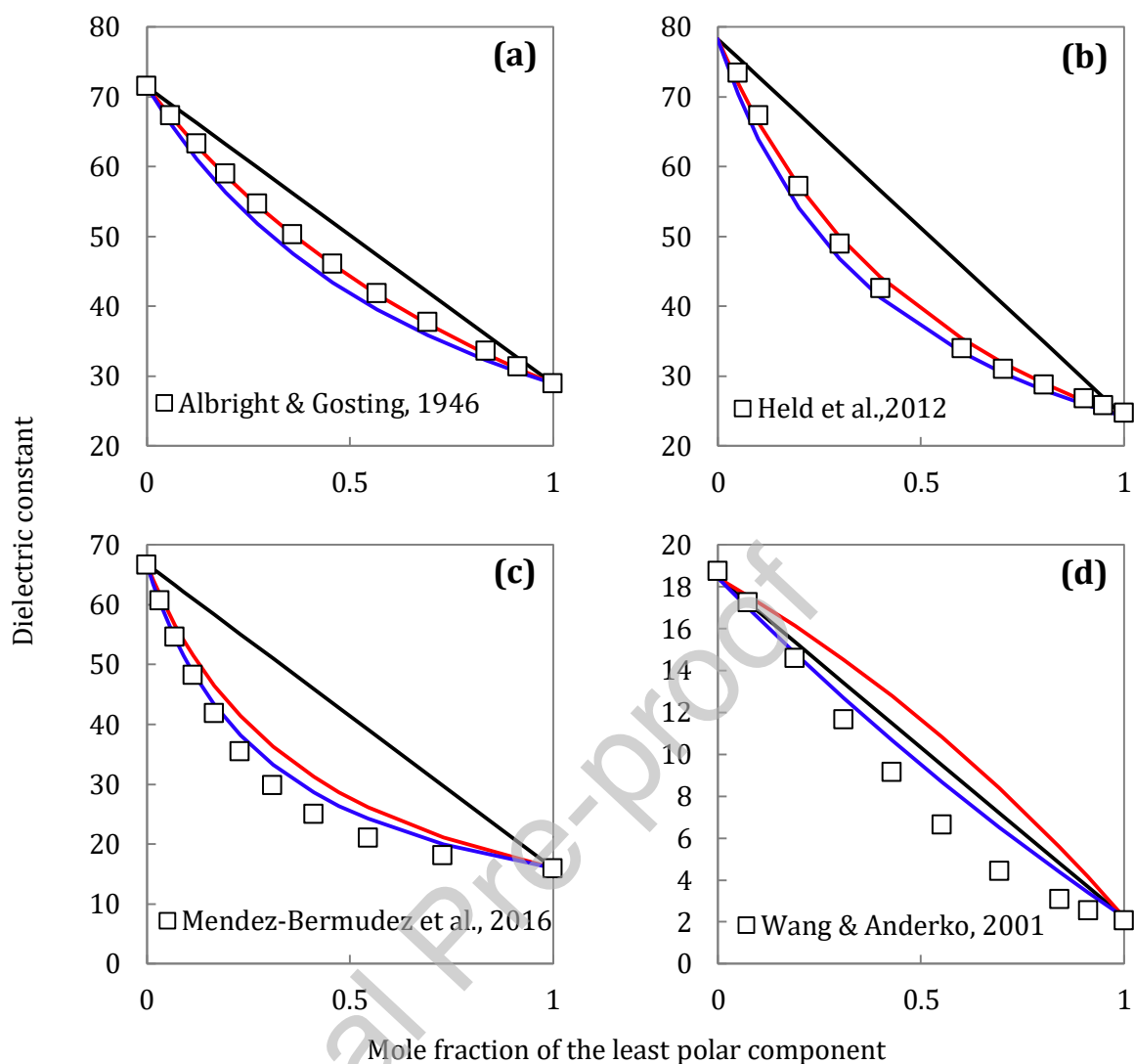


Figure 4. Dielectric constant of binary mixtures: (a) methanol* - water at 318 K, (b) ethanol* - water at 298 K, (c) 1-propanol* - water at 333 K and (d) benzene* - 1-propanol at 308 K. Points correspond to experimental data^{75,90-92}, lines to correlations with mixing rules based on mole fraction (black), weight fraction (red) and volume fraction (blue). The volume fraction has been calculated with SAFT-VR Mie EoS. The least polar component is denoted by *

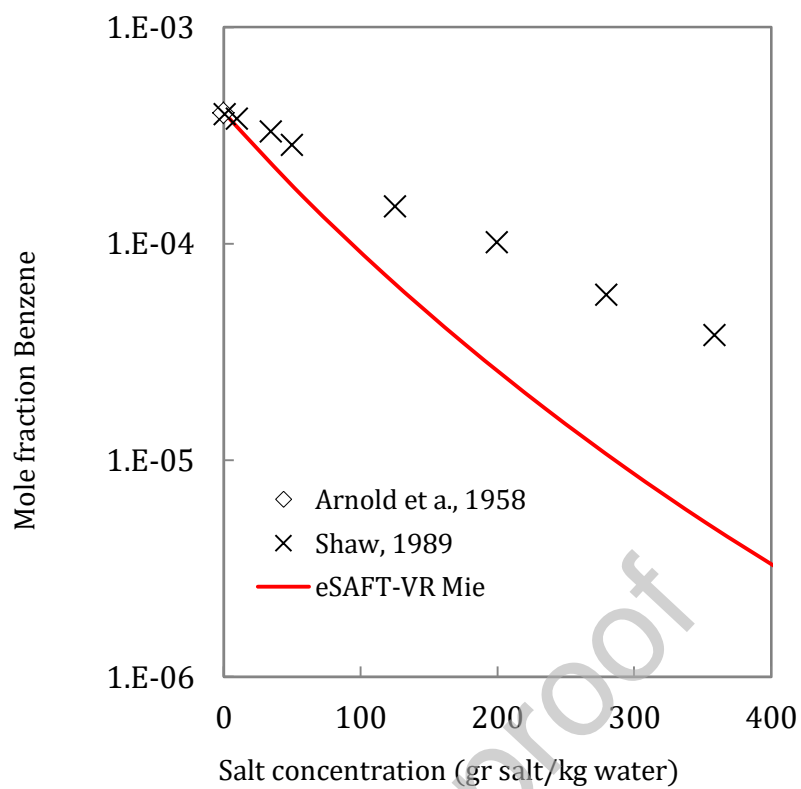


Figure 5. Solubility of benzene in water containing NaCl at atmospheric pressure and 298.15 K. Points correspond to experimental data,^{93,94} lines to eSAFT-VR Mie predictions.

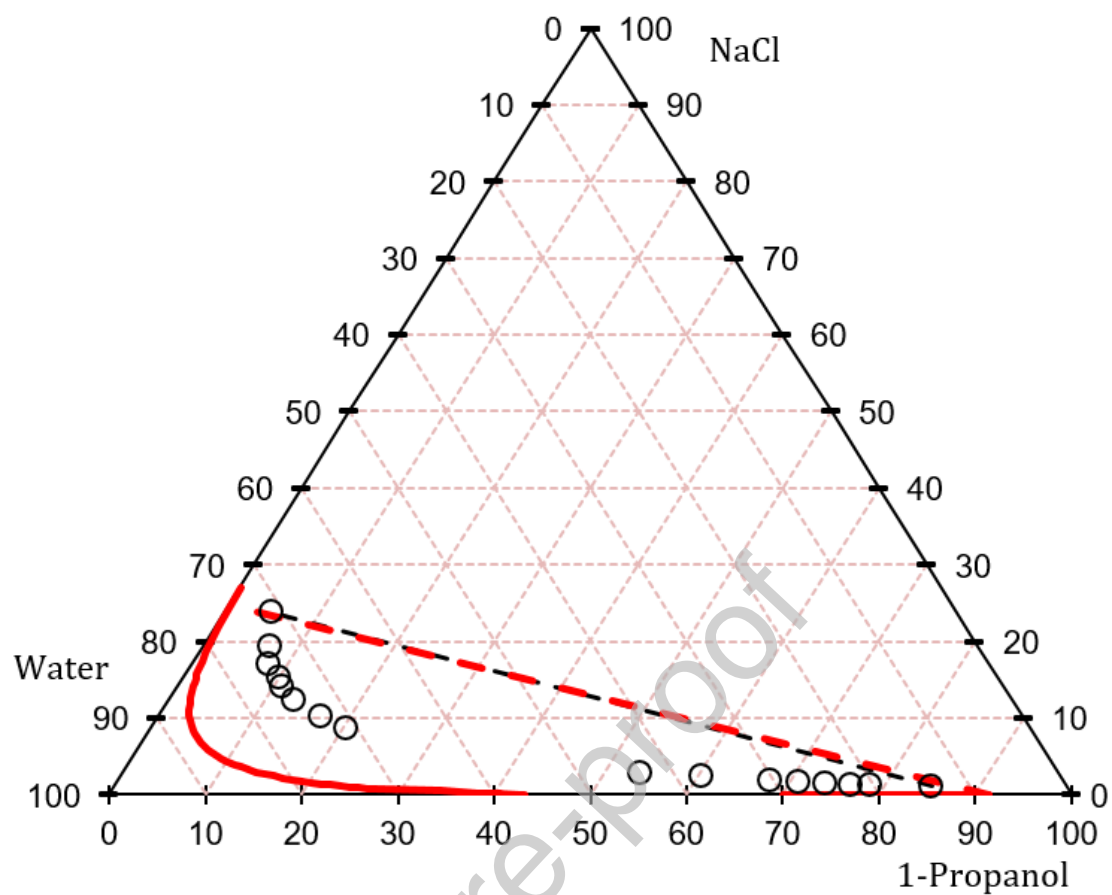


Figure 6. Phase diagram of 1-propanol - water - NaCl (w/w %) at atmospheric pressure and 298.15 K. Points correspond to experimental data,²⁵ solid red line are eSAFT-VR Mie predictions, dashed line are tie-lines from eSAFT-VR Mie

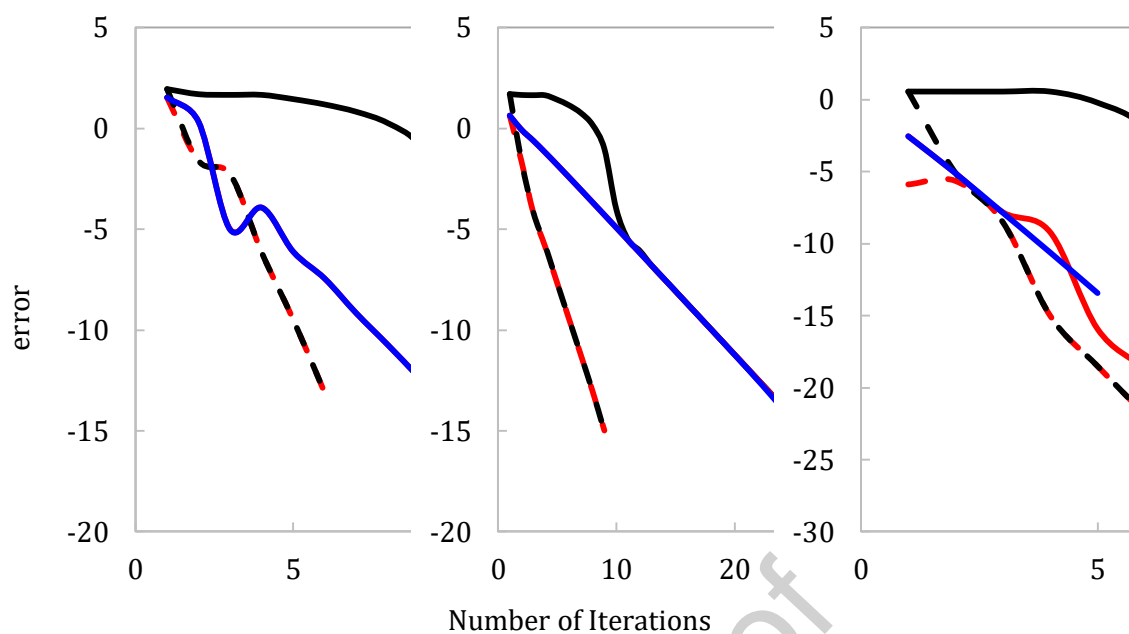


Figure 7. Error defined in eq. 86 from the different methodologies for methanol – water – KCl VLE at (a) 368.8 K and water mole fraction 0.85, (b) 356.0 K and water mole fraction 0.63 and (c) 377.6 K and water mole fraction 0.01. In all cases, pressure is 0.1 MPa and salt molality 2 mol/kg water. Blue line corresponds to the traditional RR scheme and enforcing the ionic composition of the vapor phase equal to zero, red lines to the MIA approach, black lines to the EIA. Solid lines correspond to the successive substitution, RR schemes (first order), dashed lines correspond to the full Newton schemes (second order).

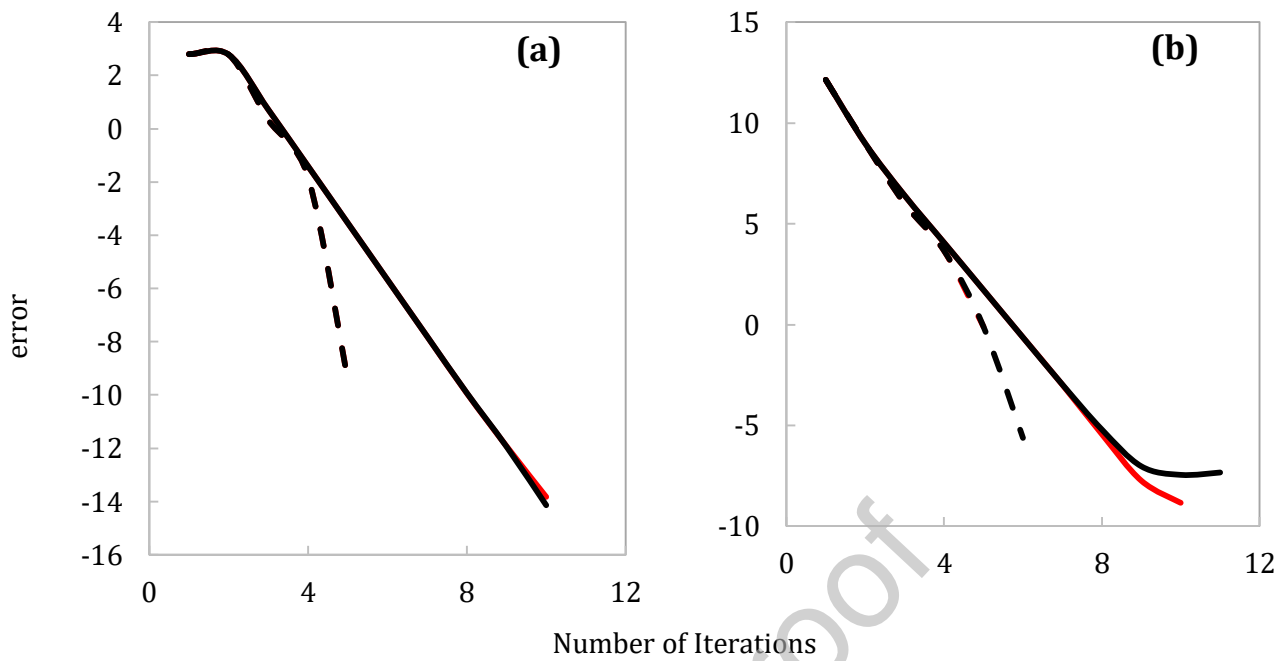


Figure 8. Error defined in eq. 86 of the different methodologies for Benzene - Water - NaCl LLE at 298.2 K and 0.1 MPa. Salt molality in the aqueous phase (a) 1.8 mole/kg water and (b) 5.9 mole/kg water. Red lines correspond to the MIA approach, black lines to the EIA. Solid lines correspond to the successive substitution, RR schemes (first order), dashed lines correspond to the full Newton schemes (second order).

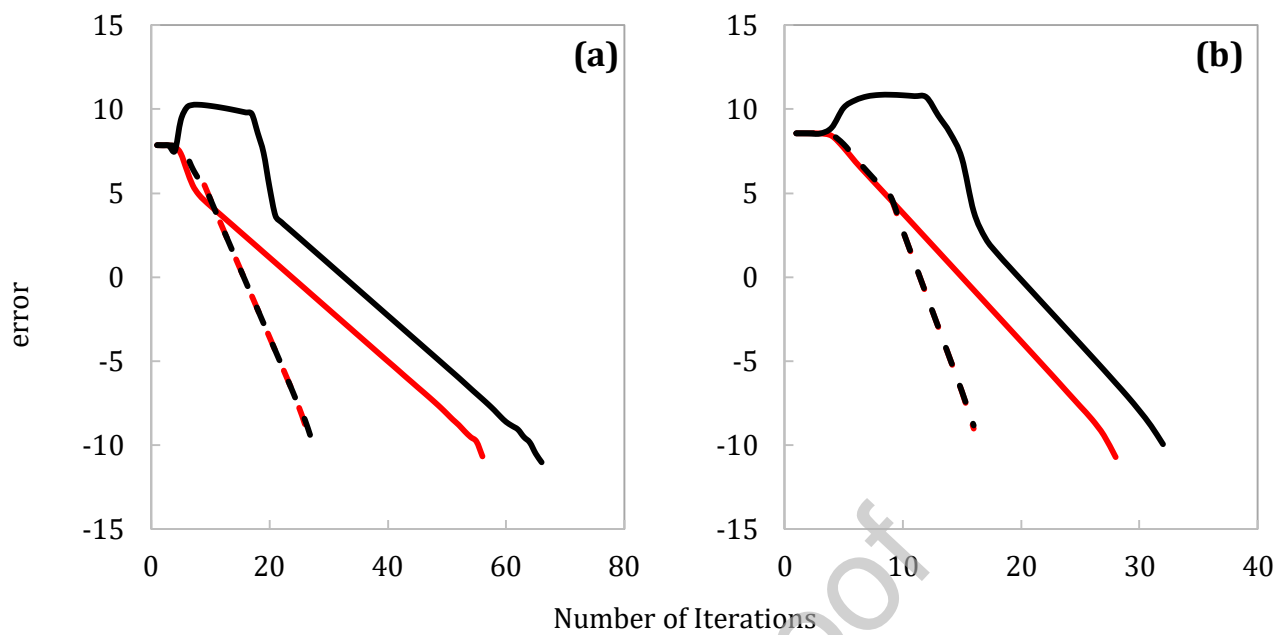


Figure 9. Error defined in eq. 86 of the different methodologies for 1-propanol – water – NaCl LLE at 298.2 K and 0.1 MPa and feed composition water: 1-propanol : NaCl w/w% (a) 37.9 : 58.2 : 3.9 and (b) 32.7 : 57.1 : 10.2 Red lines correspond to the MIA approach, black lines to the EIA. Solid lines correspond to the successive substitution, RR schemes (first order), dashed lines correspond to the full Newton schemes (second order).

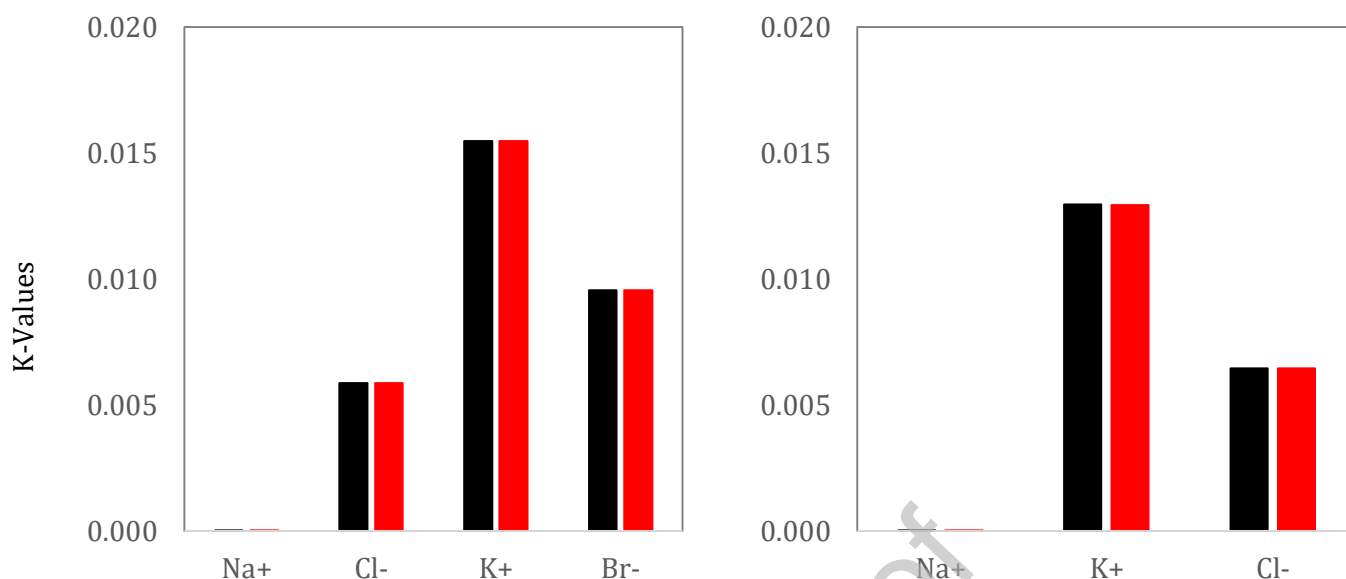


Figure 10. K -values of the ions at LLE calculated with the different methodologies for a solution of water - 1-propanol, a) NaCl, KBr and b) NaCl, KCl at 298.15 K and 0.1 MPa. Feed mole fraction (a) $z_{water} = 0.546$, $z_{1-propanol} = 0.285$, $z_{Na+} = z_{K+} = z_{Cl-} = z_{Br-} = 0.042$ and (b) $z_{water} = 0.546$, $z_{1-propanol} = 0.285$, $z_{Na+} = z_{K+} = 0.5z_{Cl-} = 0.042$. The red bars are calculated using MIA, the black bars using the EIA.

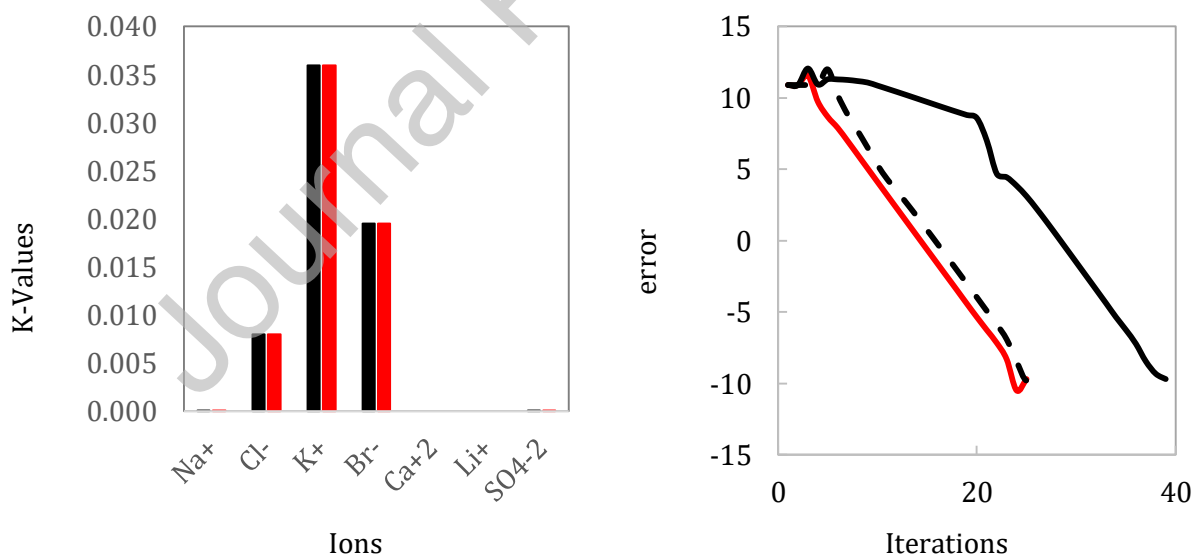


Figure 11. LLE calculation of the system water, 1-propanol - 7 ions, at 298.15 K and 0.1MPa. Feed mole fraction $z_{water} = 0.546$, $z_{1-propanol} = 0.285$, $z_{Na+} = z_{K+} = 0.5 z_{Cl-} = z_{Br-} = z_{Ca+2} = z_{Li+} = z_{SO4-2} = 0.021$. (a) K -values of the ions with the different methodologies. Red bars correspond to the MIA and black bars to the EIA. (b) Error of the different methodologies. Red lines correspond to the MIA, black lines to the EIA. Solid lines to the RR scheme, dashed lines to a Newton scheme where $d\phi/dn = 0$.

Appendix A. Necessary number of electroneutrality condition equations

When performing phase equilibrium calculations for multiple phases an important question to be addressed is whether the electro-neutrality constraint has to be applied to each of the coexisting phases. The question can be answered if the complete set of constraints is checked for linear independence.

In equilibrium calculations of two coexisting phases, the material balance for each component, written in terms of mole numbers comprises a set of linear constraints for the Gibbs free energy minimization problem⁴¹:

$$n_i^1 + n_i^2 = z_i; i = 1, 2 \dots N_C \quad (\text{A } 1)$$

where n_i^1 and n_i^2 are the mole numbers of each component in the two coexisting phases and z_i is the feed phase mole number. Assuming that the feed phase amount is 1 mole in total then z_i corresponds also to the mole fraction of the respective component. In matrix - vector notation, the system of linear material balance constraints can be written as:

$$\mathbf{A}\mathbf{n} = \mathbf{z}; (N_C \times 1) \quad (\text{A } 2)$$

$$\mathbf{A} = [\mathbf{I} \quad \mathbf{I} \quad \dots \quad \mathbf{I}]; (N_C \times N_P N_C)$$

$$\mathbf{n} = \begin{bmatrix} \mathbf{n}^1 \\ \mathbf{n}^2 \\ \vdots \\ \mathbf{n}^{N_P} \end{bmatrix}; (N_P N_C \times 1) \quad (\text{A } 3)$$

where N_P is the number of coexisting phases, N_C the number of components in the mixture and \mathbf{I} is the identity matrix with dimensions $N_C \times N_C$. For two phases in equilibrium, $N_P = 2$ and Eqs. (A 2) and (A 3) reduce to Eq. (A 1). The number of independent material balances corresponds to the number of components in the mixture and consequently $\text{rank}(\mathbf{A}) = N_C$ (matrix \mathbf{A} is full rank). Adding the electro-neutrality constraint for each phase to the set of linear constraints and writing in matrix - vector notation:

$$\mathbf{B} = \begin{bmatrix} & & \mathbf{A} & & \\ \mathbf{q}^{1T} & \mathbf{0} & \dots & \mathbf{0} & \\ \mathbf{0} & \mathbf{q}^{2T} & \dots & \mathbf{0} & \\ & \vdots & & & \\ \mathbf{0} & \mathbf{0} & \dots & \mathbf{q}^{N_P T} & \end{bmatrix}; ((N_C + N_P) \times N_P N_C) \quad (\text{A } 4)$$

$$\mathbf{B}\mathbf{n} = \begin{bmatrix} \mathbf{z} \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}; ((N_C + N_P) \times 1) \quad (\text{A } 5)$$

The linear system of Eq. (A 5) represents the total number of constraints that apply to the phase equilibrium problem when ionic species are present. Calculating the rank of matrix \mathbf{B} , we get that $\text{rank}(\mathbf{B}) = N_C + N_P - 1$. This means that matrix \mathbf{B} is not full rank and consequently the equations represented by the linear system in Eq. (A 5) are not linearly independent. For a correct representation of the phase equilibrium problem, $N_C + N_P - 1$ constraints are needed, which correspond to N_C material balances and $N_P - 1$ electro-neutrality conditions. In conclusion, for two phases in equilibrium the electro-neutrality condition must be applied only to one of the coexisting phases and the other phase will be electro-neutral as well.

Appendix B. Internal Energy in electrochemical systems

Following Münster³⁶ in Chapter XI: “Electrochemical systems”, the fundamental thermodynamic equations must be modified and generalized accordingly in order to derive suitable phase equilibrium relations that describe electrochemical systems. In this sense, the variation of internal energy can be written as:

$$\delta\tilde{U} = \delta U + \delta U^e \quad (\text{B } 1)$$

where \tilde{U} is the generalized internal energy that is comprised of two parts, the electrical one being U^e and the non-electrical one being U . The electrostatic relationship for the variation of U^e of a conductor in vacuum (assumed vacuum for simplicity) is:

$$\delta U^e = \frac{1}{4\pi} \iiint \mathbf{E} \delta \mathbf{E} dV = -\frac{1}{4\pi} \iiint \nabla \psi \delta \mathbf{E} dV \quad (\text{B } 2)$$

where ψ is the electric potential and \mathbf{E} the electric field strength. We know that:

$$\iiint \nabla(\psi \delta \mathbf{E}) dV = \iiint \nabla \psi \delta \mathbf{E} dV + \iiint \psi \nabla \cdot \delta \mathbf{E} dV \quad (\text{B } 3)$$

and $\nabla \cdot \mathbf{E} = 0$. By combining the two equations above and applying the divergence theorem of Gauss, the volume integral is transformed into a surface integral:

$$\delta U^e = -\frac{1}{4\pi} \psi \iint (\delta \mathbf{E} \cdot \mathbf{v}) ds \quad (\text{B } 4)$$

where \mathbf{v} is the unit vector, normal to the surface and $\mathbf{E} \cdot \mathbf{v} = -4\pi\sigma$, where σ is the surface charge density. The total charge of the conductor is:

$$e = \sum_{i=1}^{N_c} q_i n_i \mathcal{F} \quad (\text{B } 5)$$

where \mathcal{F} is the Faraday constant. Eq. B4 becomes:

$$\delta U^e = \psi \delta e = \psi \mathcal{F} \sum_{i=1}^{N_c} q_i \delta n_i \quad (\text{B } 6)$$

The fundamental equation for internal energy becomes:

$$d\tilde{U} = TdS - PdV + \sum_{i=1}^{N_C} (\mu_i + \psi\mathcal{F}q_i)dn_i \quad (\text{B } 7)$$

and

$$\tilde{\mu}_i = \mu_i + \psi\mathcal{F}q_i \quad (\text{B } 8)$$

The quantity $\tilde{\mu}_i$ was suggested by Guggenheim⁴³ to be called “electrochemical” potential.

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