

Prediction of the solid-liquid equilibrium of ternary and quaternary salt-water systems. Influence of the e-NRTL interaction parameters

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ABSTRACT

The aim of this work is to use the refined binary electrolyte-solvent interaction parameters of the e-NRTL model obtained in a previous paper (J.L. Valverde et al. Fluid Phase Equilibria (2022), 551, 113264) and to analyse the impact of considering the electrolyte-electrolyte interaction parameters different from zero on the prediction of solid-liquid equilibria in salt-water mixtures. For this purpose, experimental data were fitted to the complete e-NRTL model by non-linear regression. Ternary (two salts + water) and quaternary (three salts + water) systems were considered. Almost all the systems analyzed were precisely predicted by using the e-NRTL model with the electrolyte-water pairs regressed previously and electrolyte-electrolyte ones set to zero. Including the electrolyte-electrolyte binary parameters in a proper way can slightly improve the solid-liquid equilibria prediction for some of the selected systems. The $\text{Na}_2\text{SO}_4+\text{K}_2\text{SO}_4+\text{Li}_2\text{SO}_4+\text{H}_2\text{O}$ mixture was described poorly than the remainder ones computed due to the complexity of the system which exhibits the formation of multiple salts.

1. Introduction

With the rapid development of social economics, the demand of chemical products is growing up year by year [1,2]. This has led to the definition of new technologies for the utilization and extraction of several ionic salts from different liquid mineral resources (like lakes, underground brine, seawater, etc.) [1,3–34]. These fluids are usually composed of massive dissoluble salts and trace elements, such as alkali metals, alkali-earth metals, halides, and other salt-forming elements. For separating the inorganic salts from the by-product salt slurries, the phase equilibria of the related systems must be clearly established [35]. In addition, complex solutions are formed in the leaching process with the existence of many crystal forms of salts, double and multinary salts [36].

Both experimental studies, and theoretical predictions of the solid-liquid equilibria (SLE) by thermodynamic methods have been used to study multi-component water-salt systems [12,37]. There are mainly three methods for computing the equilibrium constants, which are required for describing quantitatively liquid systems where SLE of salts are established [38]. In the first method, they can be determined from the solubility of a single electrolyte in a solvent using a suitable model for describing the activity coefficients. In the second one, the equilibrium constants are obtained from the chemical potentials of the species

involved in the phase equilibrium by the Van't Hoff equation. In the last method, they are estimated from the experimental data on the ionic concentrations and the values of the activity coefficients of the different species present in solution, computed by appropriated methods.

Because the solubilities of salts in multicomponent salt-water systems are generally in high molality, it is necessary to use reliable theories for aqueous solutions of electrolytes to calculate the corresponding thermodynamic solubility constants [39]. Pitzer developed a semi-empirical thermodynamic model based on statistical mechanics and the Debye-Hückel theory [40,41]. Whitfield applied the Pitzer formula to the seawater system and calculated the activity coefficient of the major trace components [42,43]. Garcia et al. [44] used the Extended Universal QUAsiChemical model (EUNQUAC) to evaluate the thermodynamic behavior for the aqueous electrolyte systems. Hingerl et al. [45] revised EUNQUAC to model binary systems for temperatures ranging from 298 to 573 K by introducing additional adjustable parameters including effective radii for ionic species, quadratic temperature dependence of the UNQUAC binary interaction parameters, and an empirical correction term for those defined as “strongly associating electrolytes”. The model is valid for molalities up to 5 mol/kg solvent however it requires 10 species-specific binary parameters, up to 9 binary interaction parameters per solute-solute pair, and additional

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concentration dependence parameters for ternary systems. The number of adjustable parameters required in this proposal results to be a limitation for engineering calculations.

For its part, electrolyte-NRTL (e-NRTL) model consists of a generalized equation for describing the thermodynamic of mixtures containing both ionic and molecular species obtained by extension of the "classical" Non-Random Two Liquids (NRTL) model [46], previously intended for non-ionic solutions. The e-NRTL model consists of an excess Gibbs energy expression, which contains the contributions for both the long-range ion-ion interactions that exist beyond the immediate neighbourhood of a central ionic species and the local interactions that exist at the immediate neighbourhood of any central species [45–48]. The unsymmetric Pitzer-Debye-Hückel (PDH) model and the Born equation are used to represent the contribution of the long-range ion-ion interactions, and the NRTL theory is used to represent the local interactions, which is in turn normalized by infinite dilution activity coefficients to obtain an unsymmetric model. A detailed development of the e-NRTL model can be found in the seminal works by Chen et al. [47–49], in a book authored by Gmehling and col. [50] and in a previous work of our group [51]. Hossein et al. [52] have recently shown that the predictions from the e-NRTL model at high concentrations are superior to those from the Pitzer model. A recent study from Saravi et al. [53] demonstrated that the e-NRTL semi-empirical parameters are attainable from statistical mechanics and molecular simulations. e-NRTL model has been used by Chen's research group for predicting the SLE for multiple aqueous binary, ternary, and quaternary electrolyte systems [54–64]. They have shown that this model satisfactorily calculates all thermodynamic and calorimetric properties for the multicomponent systems at a range of temperatures from 273.15 to 523.15 K and salt concentrations up to saturation whenever the ionic strength of the aqueous solutions is up to 6 mol/kg, which is below the solubility limits of many electrolytes. e-NRTL model has been successful and extensively employed in computer-aided calculations of industrial applications for aqueous and mixed-solvent electrolytes [65–67]. This has been possible due to its implementation as property model in the Aspen Property/Aspen Plus program packages developed and distributed by the Aspen Technology Enterprise. Two versions of the e-NRTL model have been implemented in the referred program packages through several property methods (ELEC-NRTL, e-NRTL-RK, e-NRTL-SR, and e-NRTL-HF) that make use of the unsymmetrical original version [68,69] of the model and the more recently symmetric one [55]. Electrolyte systems can be appropriately managed in Aspen Plus by using the prior mentioned property models, which calculate molecular interactions as the NRTL method does. The Aspen Properties implementation of the e-NRTL model is flexible reducing to the classical NRTL equation when electrolyte concentration is zero.

Adjustable parameters of the e-NRTL model account, in general, for the molecule-molecule, molecule-electrolyte, and electrolyte-electrolyte interactions. They are classified into two categories: the nonrandomness factor, α_{ij} , and the binary interaction parameters, τ_{ij} , for each electrolyte-water and electrolyte-electrolyte interaction pairs when dealing with aqueous solutions. α_{ij} , having symmetric character, is often fixed at a value in the interval 0.20-0.45 (although other values are also possible), whereas τ_{ij} is asymmetric, i.e., $\tau_{ij} \neq \tau_{ji}$. Furthermore, τ_{ij} parameters reflect the temperature dependence of the corresponding interactions [48,70]. This dependence is expressed throughout the so-called binary interaction parameters in the conventional form described, for example, by the equations (1) and (2) in ref. [71].

In the previous work [71], the binary electrolyte-solvent interaction parameters of the e-NRTL model for different salts in water, using the experimental data reported in the literature, were computed, and validated. The results obtained with the refined sets of parameters along with those attained using the parameters contained in the Aspen Properties database were compared with the experimental values demonstrating that it is possible to improve the quality of the prediction of multicomponent systems with proper values of the binary

electrolyte-solvent interaction parameters, without considering electrolyte-electrolyte interactions foreseen in the original e-NRTL model.

More recently [72], the e-NRTL binary interaction parameters for alcohol-water (ethanol-water and methanol-water), electrolyte-alcohol (NaBr-methanol, NaBr-ethanol, NaCl-methanol, NaCl-ethanol, KCl-methanol and KCl-ethanol), PEG (polyethylene glycol)-water (PEG1000-, PEG4000- and PEG6000-water) and electrolyte-PEG (NaCl and KCl-PEG4000-water, KCl-PEG1000-water, LiCl-PEG4000-Water, CsCl-PEG (PEG1000, PEG4000 and PEG 6000)-Water) systems were assessed through experimental data. When dealing with mixed-solvent electrolyte solutions, for ensuring the thermodynamic consistence, the e-NRTL model incorporates the Born term [73] which includes other two parameters respect to the cases where water is the only solvent: the pure component dielectric constant coefficient of nonaqueous solvents, and the Born radius of the ionic species.

Despite the successes achieved up to now (see above-mentioned references), the quantitative e-NRTL description of the SLE remains being challenging. This is particularly critical in multinary (electrolyte + water) mixtures when several salts can precipitate and even more if they have a complex composition. In this context, the current work aims to: i) evaluate the capacity of the refined binary electrolyte-solvent interaction parameters of the e-NRTL model obtained in a previous paper [71] for the prediction of SLE of several systems reported in the literature [74], and ii) assess the impact of non-zero binary electrolyte-electrolyte interaction parameters on the accuracy of the equilibrium description.

2. Computational details

2.1. e-NRTL model

The e-NRTL model as used in this work is described next. In the NRTL expression for the local interactions, the Pitzer-Debye-Hückel's expression, and the Born's equation are added to give the following for the excess Gibbs energy [68,69,75]:

$$\frac{G_m^E}{RT} = \frac{G_m^{E,PDH}}{RT} + \frac{G_m^{E,Born}}{RT} + \frac{G_m^{E,lc}}{RT} \quad (1)$$

This leads to the unsymmetric reference state expression:

$$\ln \gamma_i = \ln \gamma_i^{PDH} + \ln \gamma_i^{Born} + \ln \gamma_i^{lc,m} \quad (2)$$

The Pitzer-Debye-Hückel's formula, normalized to mole fractions of unity for solvent and zero for electrolytes, is used to represent the long-range interaction contribution:

$$\frac{G_m^{E,PDH}}{RT} = - \left(\sum_k x_k \right) \left(\frac{1000}{M_B} \right)^{1/2} \left(\frac{4A_\phi I_x}{\rho} \right) \ln(1 + \rho I_x^{1/2}) \quad (3)$$

where:

- x_k = Mole fraction of component k
- M_B = Molecular weight of the solvent B
- A_ϕ = Debye-Hückel's parameter:

$$A_\phi = \frac{1}{3} \left(\frac{2\pi N_A d}{1000} \right)^{1/2} \left(\frac{Q_e^2}{\epsilon_w k T} \right)^{1/2} \quad (4)$$

- NA = Avogadro's number
- d = Density of solvent
- Qe = Electron charge
- ϵ_w = Dielectric constant of water
- T = Temperature
- k = Boltzmann constant
- Ix = Ionic strength (mole fraction scale):

$$I_x = \frac{1}{2} \sum_i x_i z_i^2 \quad (5)$$

x_i = Mole fraction of component i

z_i = Charge number of ion i

ρ = "Closest approach" parameter, 14.9 [76].

Taking the appropriate derivative of equation 8, an expression for the activity coefficient can then be derived:

$$\ln \gamma_i^{PDH} = - \left(\frac{1000}{M_B} \right)^{1/2} A_\rho \left[\left(\frac{2z_i^2}{\rho} \right) \ln(1 + \rho I_x^{1/2}) + \frac{z_i^2 I_x^{1/2} - 2I_x^{1/2}}{1 + \rho I_x^{1/2}} \right] \quad (6)$$

The Born's equation is used to account for the Gibbs' energy of transfer of ionic species from the infinite dilution state in a mixed solvent to the infinite dilution state in aqueous phase.

$$\frac{G_m^{E,Born}}{RT} = \frac{Q_e^2}{2kT} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_w} \right) \left(\sum_i x_i z_i^2 \right) 10^{-2} \quad (7)$$

where: r_i = Born's radius, which can be obtained from reference [77].

The expression for the activity coefficient can be derived from equation (7):

$$\ln \gamma_i^{Born} = \frac{Q_e^2}{2kT} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_w} \right) \left(\frac{z_i^2}{r_i} \right) 10^{-2} \quad (8)$$

By introducing $X_i = x_i C_i$, where $C_i = |z_i|$ for ions, and $C_i = 1$ for molecules, the e-NRTL model can be extended to handle multicomponent systems. Thus, the activity coefficient in the scale of molar fraction equation (symmetric convention) for molecular components is given by:

$$\begin{aligned} \ln \gamma_B^{lc} = & \frac{\sum_j X_j G_{jB} \tau_{jB}}{\sum_k X_k G_{kB}} + \sum_{B'} \frac{X_{B'} G_{BB'}}{\sum_k X_k G_{kB'}} \left(\tau_{BB'} - \frac{\sum_k X_k G_{kB'} \tau_{kB'}}{\sum_k X_k G_{kB'}} \right) \\ & + \sum_c \sum_a \frac{X_a}{\sum_a X_a} \frac{X_c G_{Bc,a'}}{\sum_{k \neq c} X_k G_{kc,a'}} \left(\tau_{Bc,a'} - \frac{\sum_k X_k G_{kc,a'} \tau_{kc,a'}}{\sum_k X_k G_{kc,a'}} \right) \\ & + \sum_a \sum_c \frac{X_c}{\sum_c X_c} \frac{X_a G_{Ba,c'}}{\sum_{k \neq a} X_k G_{ka,c'}} \left(\tau_{Bc,c'} - \frac{\sum_k X_k G_{ka,c'} \tau_{ka,c'}}{\sum_k X_k G_{ka,c'}} \right) \end{aligned} \quad (9)$$

The activity coefficient equation for cations is given by:

$$\begin{aligned} \frac{1}{z_c} \ln \gamma_c^{lc} = & \sum_a \left(\frac{X_a}{\sum_a X_a} \right) \frac{\sum_k X_k G_{ka,c'} \tau_{jka,c'}}{\sum_k X_k G_{ka,c'}} \\ & + \sum_{B'} \frac{X_{B'} G_{cB'}}{\sum_k X_k G_{kB'}} \left(\tau_{cB'} - \frac{\sum_k X_k G_{kB'} \tau_{kB'}}{\sum_k X_k G_{kB'}} \right) \\ & + \sum_a \sum_c \frac{X_c}{\sum_c X_c} \frac{X_a G_{ca,c'}}{\sum_{k \neq a} X_k G_{ka,c'}} \left(\tau_{ca,c'} - \frac{\sum_k X_k G_{ka,c'} \tau_{ka,c'}}{\sum_k X_k G_{ka,c'}} \right) \end{aligned} \quad (10)$$

The activity coefficient equation for anions is given by:

$$\begin{aligned} \frac{1}{z_a} \ln \gamma_a^{lc} = & \sum_c \left(\frac{X_c}{\sum_c X_c} \right) \frac{\sum_k X_k G_{ka,c'} \tau_{jka,c'}}{\sum_k X_k G_{ka,c'}} \\ & + \sum_{B'} \frac{X_{B'} G_{aB'}}{\sum_k X_k G_{kB'}} \left(\tau_{aB'} - \frac{\sum_k X_k G_{kB'} \tau_{kB'}}{\sum_k X_k G_{kB'}} \right) \\ & + \sum_c \sum_a \frac{X_a}{\sum_a X_a} \frac{X_c G_{ac,c'}}{\sum_{k \neq c} X_k G_{kc,c'}} \left(\tau_{ac,c'} - \frac{\sum_k X_k G_{kc,c'} \tau_{kc,c'}}{\sum_k X_k G_{kc,c'}} \right) \end{aligned} \quad (11)$$

where:

$$G_{cB} = \frac{\sum_a X_a G_{ca,B}}{\sum_a X_a} \therefore G_{aB} = \frac{\sum_c X_c G_{ca,B}}{\sum_c X_c} \quad (12)$$

$$\alpha_{Bc} = \alpha_{cB} = \frac{\sum_a X_a \alpha_{Bc,ca}}{\sum_a X_a} \therefore \alpha_{Ba} = \alpha_{aB} = \frac{\sum_c X_c \alpha_{Bc,ca}}{\sum_c X_c} \quad (13)$$

$$\tau_{cB} = -\frac{\ln G_{cB}}{\alpha_{cB}} \therefore \tau_{aB} = -\frac{\ln G_{aB}}{\alpha_{cB}} \quad (14)$$

$$\tau_{Ba,ca} = \tau_{aB} - \tau_{ca,B} + \tau_{B,ca} \therefore \tau_{Bc,ac} = \tau_{cB} - \tau_{ca,B} + \tau_{B,ca} \quad (15)$$

On the other hand, from the equations (9-11) is possible to evaluate the activity coefficients at infinite dilution:

$$\ln \gamma_B^{lc,\infty} = \frac{\sum_j X_j G_{jB} \tau_{jB}}{\sum_k X_k G_{kB}} + \sum_{B'} \frac{X_{B'} G_{BB'}}{\sum_k X_k G_{kB'}} \left(\tau_{BB'} - \frac{\sum_k X_k G_{kB'} \tau_{kB'}}{\sum_k X_k G_{kB'}} \right) \quad (16)$$

$$\frac{1}{z_c} \ln \gamma_c^{lc,\infty} = \sum_a \left(\frac{X_a}{\sum_a X_a} \right) \frac{\sum_k X_k G_{ka,c'} \tau_{jka,c'}}{\sum_k X_k G_{ka,c'}} + \sum_{B'} \frac{X_{B'} G_{cB'}}{\sum_k X_k G_{kB'}} \tau_{cB'} \quad (17)$$

$$\frac{1}{z_a} \ln \gamma_a^{lc,\infty} = \sum_c \left(\frac{X_c}{\sum_c X_c} \right) \frac{\sum_k X_k G_{ka,c'} \tau_{jka,c'}}{\sum_k X_k G_{ka,c'}} + \sum_{B'} \frac{X_{B'} G_{aB'}}{\sum_k X_k G_{kB'}} \tau_{aB'} \quad (18)$$

The nonrandomness factor is often set a priori to a fixed value (0.2 for electrolyte-solvent-pairs and 0.3 for solvent-solvent-pairs and solvent-solute-pairs). This way, it is possible to evaluate the unsymmetric convention-based activity coefficients:

$$\gamma_i^{lc,x} = \frac{\gamma_i^{lc}}{\gamma_i^{lc,\infty}} \quad (19)$$

Finally, the activity coefficient in the scale of molalities, $\gamma_i^{lc,m}$ can be computed through the following expression [78]:

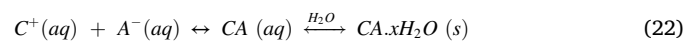
$$\gamma_i^{lc,x} = \gamma_i^{lc,m} \left(1 + \frac{\sum_{c,a,B} m_j M_{solvi}}{1000} \right) \quad (20)$$

Finally, the activity of water can be computed as follows:

$$a_{water} = \gamma_{water}^{lc} x_{water} \quad (21)$$

2.2. Thermodynamic formulation of the SLE

Thermodynamic description of the SLE entails not only the phase but also the chemical equilibrium which, for example, can take the simplified form given by the equation (22). The chemical equilibrium of dissociation or precipitation determines the ionic concentration in the solution.



where C and A designate any cation and anion, respectively.

In this formalism, the salt solubility is quantified throughout the equilibrium constant for the reaction (22) in terms of the solubility product constant, K_{sp} . It can be calculated by equation (23) [60,72]:

$$K_{sp} = \left\{ \prod_i (m_i \gamma_i)^{\nu_i} \right\} \cdot a_w^{\nu_w} \quad (23)$$

where: m_i is the saturation molality of ion i , γ_i is the activity coefficient of ion i ; a_w is the activity of water, and ν_i and ν_w are the corresponding reaction stoichiometric coefficients of ion i and water, respectively.

The formulation given by equation (23) can be extended to systems with several ionic species and complex salts to precipitate. This suggests that the set of chemical reactions selected for describing the precipitation processes in complex mixtures plays an important role not only in the thermodynamic description of the SLE but also in the capacity for correctly estimating the activity coefficients.

In the current work, as a rule, ionic concentrations in equation (23) have been taken from the corresponding literature references whereas the activity coefficients have been calculated using the e-NRTL equation.

When calculating ternary systems, the equilibrium constants for both solids were determined from the solubility of the single electrolytes in water using the e-NRTL model with the binary interaction parameters for each electrolyte-water pair for describing the activity coefficients. Tables S1 to S4 list the electrolyte-solvent interaction parameters pairs for each system. In the cases of the quaternary mixtures, the equilibrium constants for the solubility of single electrolytes in water were also determined by either using the e-NRTL model and taking the values reported in each of the papers referenced. Tables S6 to S11 list the electrolyte-electrolyte interaction parameters pairs for each system.

Experimental data of both the ternary and the quaternary systems considered in the current work were taken from literature as shown in Table 1.

The results of the SLE calculations for the quaternary systems (three salts + water) were consigned using the Jänecke dry-salt indexes:

$$J(\text{salt } i) = \frac{w_{\text{salt } i}}{w_{\text{salt } 1} + w_{\text{salt } 2} + w_{\text{salt } 3}} \times 100 \quad (24)$$

where $w_{\text{salt } j}$ is the mass fraction of salt j in solution.

2.3. e-NRTL parameters

The e-NRTL binary interaction parameters used in the current work, τ_{ij} , for each electrolyte-water system were regressed from experimental mean ionic coefficient data of aqueous electrolyte at 298.15 K and reported in a previous paper [71]. Table 2 lists the values of the binary electrolyte-water interaction parameters used in this manuscript and the maximum value of molality of the corresponding salt in solution employed for their evaluation [71].

To evaluate the impact of considering the values of the e-NRTL electrolyte-electrolyte pair interaction parameters different from zero on the prediction of the different equilibria, experimental data were fitted

Table 1

Source of experimental data on the ternary and quaternary systems computed in the current work.

TERNARY SYSTEMS			
System	T (K)	Maximum molality in solution	Reference
NaCl+KCl+H ₂ O	298.15	NaCl: 6.163 mol/kg KCl: 4.841 mol/kg	[79]
NaCl+SrCl ₂ +H ₂ O	288.15	NaCl: 6.122 mol/kg SrCl ₂ : 3.204 mol/kg	[15]
KCl+SrCl ₂ +H ₂ O	288.15	KCl: 4.414 mol/kg SrCl ₂ : 3.204 mol/kg	[15]
KBr+SrBr ₂ +H ₂ O	288.15	KBr: 5.763 mol/kg SrBr ₂ : 4.283 mol/kg	[18]
LiCl+Li ₂ SO ₄ +H ₂ O	288.15	LiCl: 18.650 mol/kg Li ₂ SO ₄ : 3.298 mol/kg	[24]
QUATERNARY SYSTEMS			
System	T (K)	Maximum molality in solution	Reference
KBr+MgBr ₂ +SrBr ₂ +H ₂ O	298.15	KBr: 1.212 mol/kg MgBr ₂ : 5.498 mol/kg SrBr ₂ : 4.100 mol/kg	[11]
NaBr+MgBr ₂ +SrBr ₂ +H ₂ O	298.15	NaBr: 4.639 mol/kg MgBr ₂ : 5.367 mol/kg SrBr ₂ : 2.943 mol/kg	[11]
NaBr+KBr+SrBr ₂ +H ₂ O	298.15	NaBr: 8.780 mol/kg KBr: 1.309 mol/kg SrBr ₂ : 4.101 mol/kg	[11]
NaCl+KCl+SrCl ₂ +H ₂ O	288.15	NaCl: 5.221 mol/kg KCl: 1.799 mol/kg SrCl ₂ : 3.939 mol/kg	[2]
LiCl+KCl+SrCl ₂ +H ₂ O	298.15	LiCl: 19.950 mol/kg KCl: 1.600 mol/kg SrCl ₂ : 3.373 mol/kg	[10]
Na ₂ SO ₄ +K ₂ SO ₄ +Li ₂ SO ₄ +H ₂ O	288.15	Na ₂ SO ₄ : 2.518 mol/kg K ₂ SO ₄ : 1.715 mol/kg Li ₂ SO ₄ : 6.623 mol/kg	[22]

Table 2

Values of the binary electrolyte-solvent interaction parameters for each electrolyte-water system and the maximum value of molality of the corresponding salt in solution used for their evaluation [71].

Salt	Values of the binary interaction parameters	Maximum value of molality
NaCl	$\tau_{\text{NaCl,H}_2\text{O}} = -4.591$; $\tau_{\text{H}_2\text{O,NaCl}} = 9.002$	6.0
KCl	$\tau_{\text{KCl,H}_2\text{O}} = -4.117$; $\tau_{\text{H}_2\text{O,KCl}} = 8.085$	4.8
SrCl ₂	$\tau_{\text{SrCl}_2,\text{H}_2\text{O}} = -5.079$; $\tau_{\text{H}_2\text{O,SrCl}_2} = 10.023$	4.0
KBr	$\tau_{\text{KBr,H}_2\text{O}} = -4.136$; $\tau_{\text{H}_2\text{O,KBr}} = 8.072$	5.5
SrBr ₂	$\tau_{\text{SrBr}_2,\text{H}_2\text{O}} = -4.806$; $\tau_{\text{H}_2\text{O,SrBr}_2} = 9.082$	2.0
MgBr ₂	$\tau_{\text{MgBr}_2,\text{H}_2\text{O}} = -5.348$; $\tau_{\text{H}_2\text{O,MgBr}_2} = 10.350$	2.5
NaBr	$\tau_{\text{NaBr,H}_2\text{O}} = -4.570$; $\tau_{\text{H}_2\text{O,NaBr}} = 8.811$	4.0
LiCl	$\tau_{\text{LiCl,H}_2\text{O}} = -5.242$; $\tau_{\text{H}_2\text{O,LiCl}} = 10.300$	6.0
Na ₂ SO ₄	$\tau_{\text{Na}_2\text{SO}_4,\text{H}_2\text{O}} = -3.718$; $\tau_{\text{H}_2\text{O,Na}_2\text{SO}_4} = 7.581$	4.0
K ₂ SO ₄	$\tau_{\text{K}_2\text{SO}_4,\text{H}_2\text{O}} = -4.310$; $\tau_{\text{H}_2\text{O,K}_2\text{SO}_4} = 8.840$	0.7
Li ₂ SO ₄	$\tau_{\text{Li}_2\text{SO}_4,\text{H}_2\text{O}} = -4.058$; $\tau_{\text{H}_2\text{O,Li}_2\text{SO}_4} = 7.914$	3.0

by non-linear regression to the complete e-NRTL model. It was not considered a temperature dependence of the interaction parameters as it was shown in a previous paper since its impact on the results is very weak if compared to that observed for Pitzer model [51,68,69]. The nonrandomness factor for the electrolyte-electrolyte pair interaction parameters was fixed at 0.2. The objective function (χ^2) to be minimized in each case for fitting experimental data (*exp*) to theoretical or predicted (*th*) ones is as follows:

$$\chi^2 = \left[\sum_{i=1}^M \sum_{j=1}^S \left(m_{ji}^{\text{exp}} - m_{ji}^{\text{th}} \right)^2 \right] \quad (25)$$

where M is the number of data considered, S is the number of salts that results from the combination of cations and anions present in solution, m_{ji} is the molality of equilibrated solution for salt j and run i . An analysis of variance (ANOVA) for the model and the corresponding parameters was included in the computational process.

For reducing the number of parameters to be fitted, the following assumption was followed:

$$\tau_{ca,c'a} = -\tau_{c'a,ca} \quad (26)$$

$$\tau_{ca,cd} = -\tau_{cd,ca} \quad (27)$$

The binary electrolyte-electrolyte interaction pairs regressed for all the systems considered are given as Supplementary Material as already mentioned.

This way, results labelled as e-NRTL BIN will be the predictions made by using the refined e-NRTL binary interaction parameters for each electrolyte-water pair reported in a previous paper [71], setting the electrolyte-electrolyte pairs ones to zero. Meanwhile, those identified with e-NRTL BIN + EPairs will be the prediction made by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature.

2.4. Validation of the binary parameters

Although in the previous paper [71], the quality of the regressions accomplished for obtaining the refined binary electrolyte-water interaction parameters was statistically demonstrated, in the current work some binary systems are used as validation of the parameters used here. Due to the high quality of the binary parameters stored in the Aspen Properties databases (release 11) and listed in reference [71], the predictions realized with Aspen Plus are also shown for comparison. All the remainder calculations were performed with a home-made MS Excel-VBA application described previously [71].

3. Results and discussion

3.1. Impact of the values of binary electrolyte-water interaction parameters, τ_{ij}

Fig.s 1-6 show the predicted molality mean ionic activity of some of the pure salts considered in this study (KCl, NaBr, MgBr₂, Li₂SO₄, LiCl and LiBr, respectively) vs. the molality of the salt in the solutions previously computed [71]. The comparison of the predictions with different binary parameters (those obtained previously [71] and the stored in the Aspen Property databases) demonstrates that it is possible improving the quality of the prediction of multicomponent systems with proper values of the binary electrolyte interaction parameters, without considering electrolyte-electrolyte interactions foreseen in the original e-NRTL model.

As already described in the previous paper [71], not all the electrolyte-water and water-electrolyte interaction pairs, $\tau_{salt,water}$ and $\tau_{water,salt}$, included in the Aspen Property database are able to correctly predict the experimental data. It must be highlighted from the above-mentioned previous study [71] that the values of the interaction pairs evaluated by non-linear regression using different strategies were very similar.

3.2. Liquid-solid equilibria. Ternary systems

The predictions of several ternary systems (two salts + water) with procedures e-NRTL BIN and e-NRTL BIN + EPairs (as above defined) are shown in Fig.s 7-11. Experimental data were taken from literature according to references included in Table 1. As a rule, e-NRTL BIN property model ensures a reasonably good prediction of the SLE of the systems considered in this work. For example, the invariant points of all the ternary systems studied are predicted with low deviations respect to the experimental data as shown in Table 3. Thus, it is observed a good agreement between the experimental and predicted values of the invariant points for all the ternary systems when e-NRTL BIN is used. In the case of the NaCl-KCl-H₂O and LiCl-Li₂SO₄-H₂O the e-NRTL BIN predictions are so good as those reached including the electrolyte-electrolyte interaction pairs (e-NRTL BIN + EPairs).

Nevertheless, the calculation of the SLE for the remainder systems studied in this work (NaCl+SrCl₂+H₂O, KCl+SrCl₂+H₂O and KBr+SrBr₂+H₂O) suggests that including the binary electrolyte-

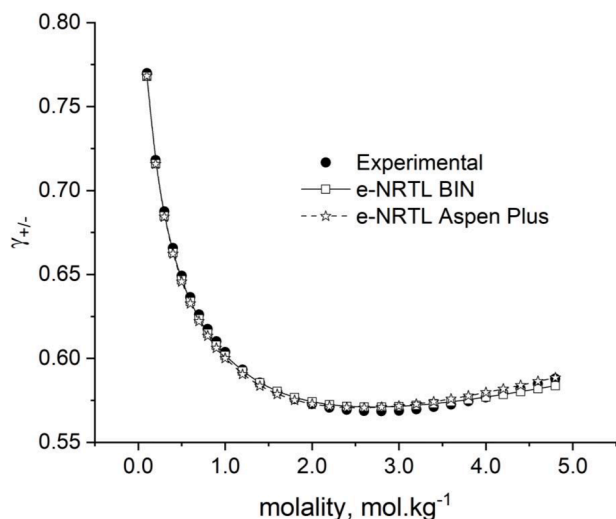


Fig. 1. Comparison of experimental [74] and predicted mean ionic activity coefficients of KCl at 298.15 K. Experimental represents the experimental data; e-NRTL BIN is the prediction made with the refined parameters obtained in [71]; and e-NRTL Aspen Plus is the estimation done with the parameters stored in the Aspen Properties database.

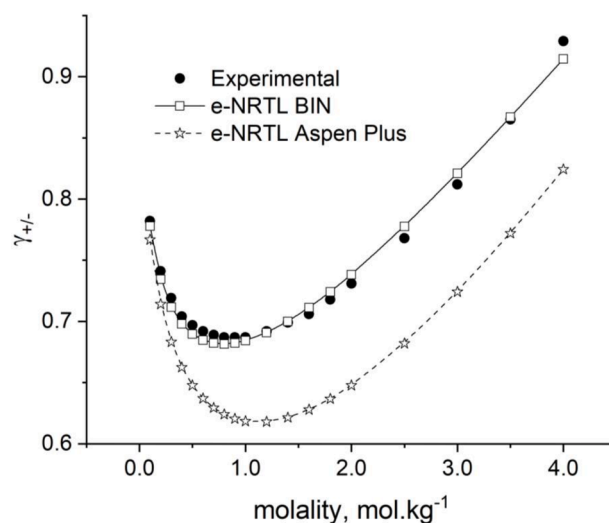


Fig. 2. Comparison of experimental [74] and predicted mean ionic activity coefficients of NaBr at 298.15 K. Experimental represents the experimental data; e-NRTL BIN is the prediction made with the refined parameters obtained in [71]; and e-NRTL Aspen Plus is the estimation done with the parameters stored in the Aspen Properties database.

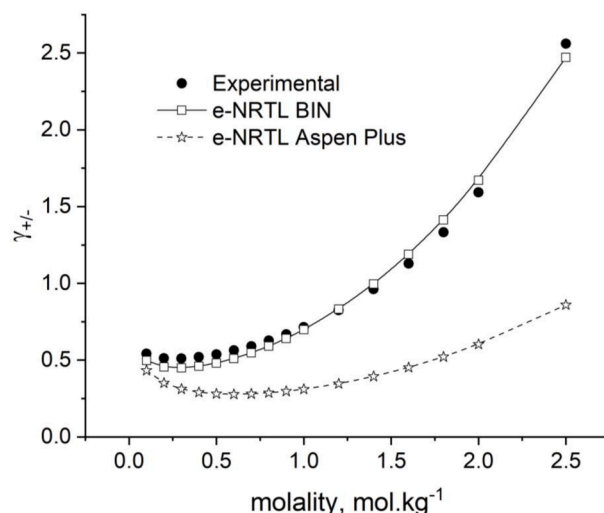


Fig. 3. Comparison of experimental [74] and predicted mean ionic activity coefficients of MgBr₂ at 298.15 K. Experimental represents the experimental data; e-NRTL BIN is the prediction made with the refined parameters obtained in [71]; and e-NRTL Aspen Plus is the estimation done with the parameters stored in the Aspen Properties database.

electrolyte interactions parameters (e-NRTL BIN + EPairs) slightly improves this kind of prediction. Tables S1 to S5 contain the electrolyte-electrolyte parameters for the systems depicted in Fig.s 7-11, respectively.

3.3. Liquid-solid equilibria. Quaternary systems

The predictions of quaternary systems (three salts + water) with procedures e-NRTL BIN and e-NRTL BIN + EPairs are shown in Fig.s 12-17 according to the value of the Jänecke dry-salt indexes. Tables S6 to S11 list the electrolyte-electrolyte interaction parameter pairs used for each system in the second calculations.

As a rule, both procedures predict in similar way the experimental data regardless the values of the electrolyte-electrolyte pair interaction parameters. No improvement on the quality of the prediction was

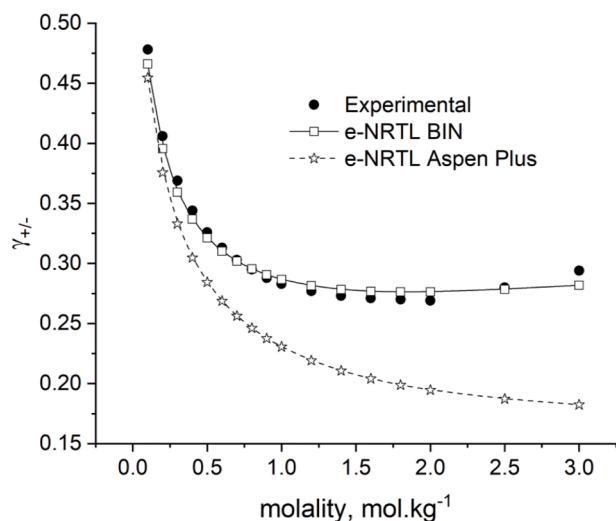


Fig. 4. Comparison of experimental [74] and predicted mean ionic activity coefficients of Li_2SO_4 at 298.15 K. Experimental represents the experimental data; e-NRTL BIN is the prediction made with the refined parameters obtained in [71]; and e-NRTL Aspen Plus is the estimation done with the parameters stored in the Aspen Properties database.

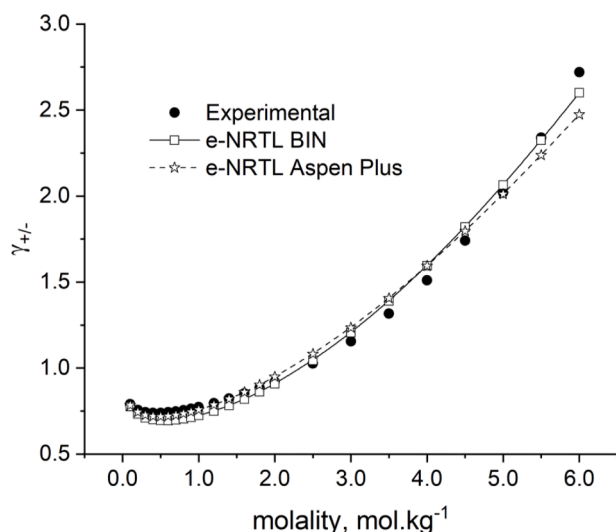


Fig. 5. Comparison of experimental [74] and predicted mean ionic activity coefficients of LiCl at 298.15 K. Experimental represents the experimental data; e-NRTL BIN is the prediction made with the refined parameters obtained in [71]; and e-NRTL Aspen Plus is the estimation done with the parameters stored in the Aspen Properties database.

observed when considered non-zero values for these parameters. In the case of system $\text{NaCl}+\text{KCl}+\text{SrCl}_2+\text{H}_2\text{O}$ the previous observation is also satisfied but the prediction reached with both procedures was a little bit worse. The worst results within the six systems studied here corresponded to the $\text{Na}_2\text{SO}_4+\text{K}_2\text{SO}_4+\text{Li}_2\text{SO}_4+\text{H}_2\text{O}$ one even using the e-NRTL model with both parameters sets i.e., no improvement on the quality of the prediction is observed when considered non-zero values for electrolyte-electrolyte parameters. This fact could be mainly associated to two factors: i) the complexity of the equilibria raised. The low solubility of the sulphates along with the presence of three different cations enables the formation of several salts, including some of multiple composition. The preference to precipitate these last salts could be explained by the similitude of the metals, belonging to the same group in the periodic table. Additionally, it is important recognizing: ii) the uncertainty in the values of the solubility products of the multiple salts

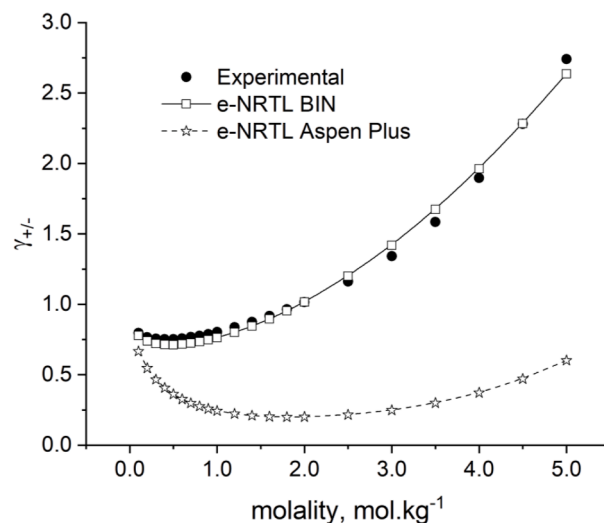


Fig. 6. Comparison of experimental [74] and predicted mean ionic activity coefficients of LiBr at 298.15 K. Experimental represents the experimental data; e-NRTL BIN is the prediction made with the refined parameters obtained in [71]; and e-NRTL Aspen Plus is the estimation done with the parameters stored in the Aspen Properties database.

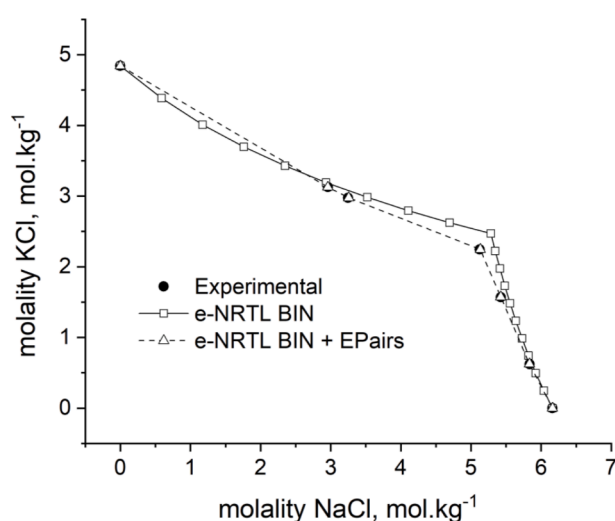


Fig. 7. Phase diagram of the ternary system $\text{NaCl}-\text{KCl}-\text{H}_2\text{O}$ at 298.15 K. Experimental represents the experimental data [79]; e-NRTL BIN is the prediction made with the e-NRTL model with the refined parameters obtained in [71] and electrolyte-electrolyte pair interaction parameters set to zero; and e-NRTL BIN + EPairs is the estimation done by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature. Two equilibrium solid phases were considered: NaCl and KCl .

taken from the literature. In a recent paper [79], an association-based activity coefficient model, related to the e-NRTL model, was developed which explicitly considered the solution nonideality due to associations among ions and solvent species and improved the accuracy of the e-NRTL model for strongly associating electrolyte solutions. That is the case for anions with greater association strengths, like sulphates, with eight water molecules in the inner shell, which are more likely to form more ion pairs and therefore lower the activity coefficients.

Summarizing, regardless the quality of the prediction, the impact of considering values of the electrolyte-electrolyte pair interaction parameters different from zero is not so evident as could be expected, being other effects associated to the complexity of the system considered more

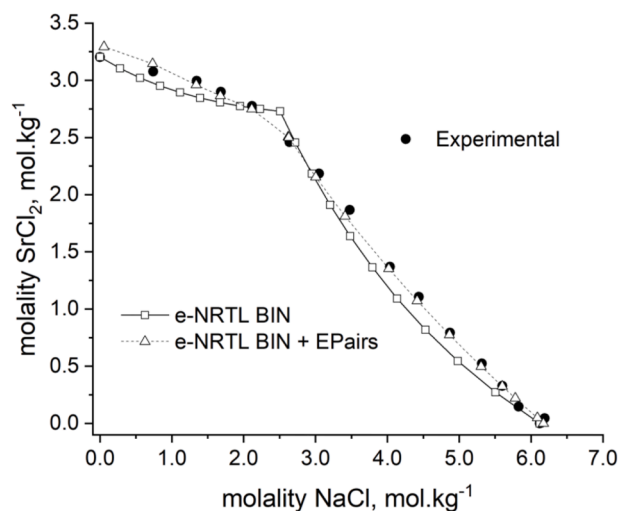


Fig. 8. Phase diagram of the ternary system NaCl-SrCl₂-H₂O at 288.15 K. Experimental represents the experimental data [15]; e-NRTL BIN is the prediction made with the e-NRTL model with the refined parameters obtained in [71] and electrolyte-electrolyte pair interaction parameters set to zero; and e-NRTL BIN + EPairs is the estimation done by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature. Two equilibrium solid phases were considered: NaCl and SrCl₂.

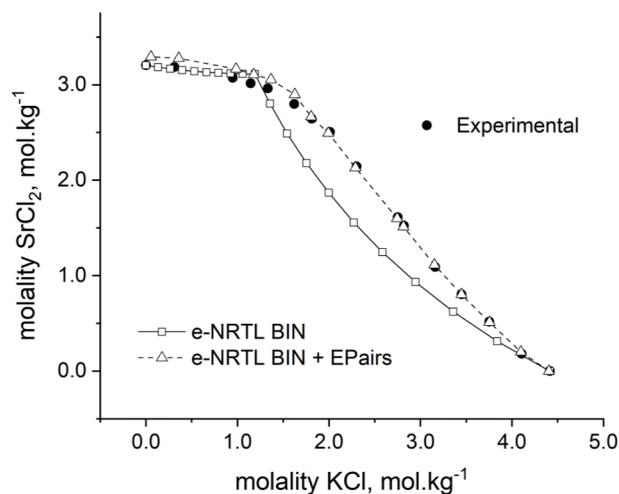


Fig. 9. Phase diagram of the ternary system KCl-SrCl₂-H₂O at 288.15 K. Experimental represents the experimental data [15]; e-NRTL BIN is the prediction made with the e-NRTL model with the refined parameters obtained in [71] and electrolyte-electrolyte pair interaction parameters set to zero; and e-NRTL BIN + EPairs is the estimation done by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature. Two equilibrium solid phases were considered: KCl and SrCl₂•6H₂O.

remarkable. That means that the use of the refined electrolyte-water pairs and electrolyte-electrolyte ones set to zero are enough to get a reasonable prediction of complex systems as liquid-solid equilibria are.

On the other hand, as seen in Tables S1 to S11, different values of the same electrolyte-electrolyte pair interaction parameters were obtained by non-linear regression as a function of a specific set of experimental data considered. Anyway, although not all the parameters evaluated by non-linear regression are statistical meaningful, all the models are.

These results corroborate those reported in a previous paper focused on the prediction of multicomponent electrolyte systems and would demonstrate that is possible to predict the equilibria of electrolyte

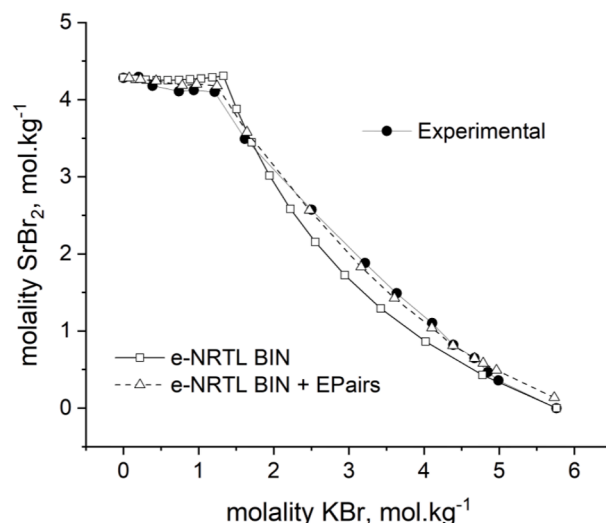


Fig. 10. Phase diagram of the ternary system KBr-SrBr₂-H₂O at 288.15 K. Experimental represents the experimental data [18]; e-NRTL BIN is the prediction made with the e-NRTL model with the refined parameters obtained in [71] and electrolyte-electrolyte pair interaction parameters set to zero; and e-NRTL BIN + EPairs is the estimation done by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature. Two equilibrium solid phases were considered: KBr and SrBr₂•6H₂O.

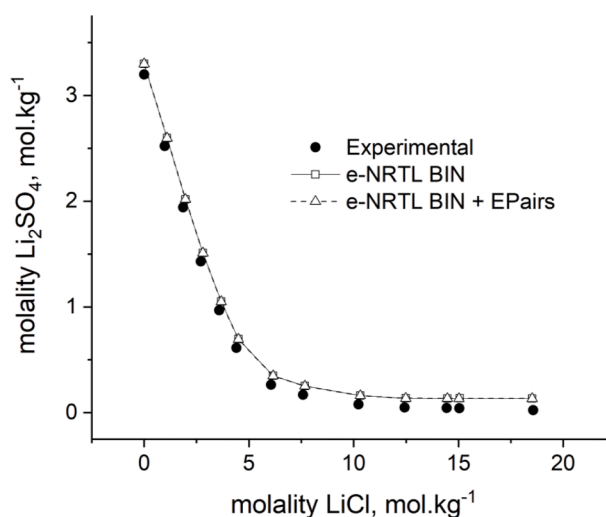


Fig. 11. Phase diagram of the ternary system LiCl-Li₂SO₄-H₂O at 288.15 K. Experimental represents the experimental data [24]; e-NRTL BIN is the prediction made with the e-NRTL model with the refined parameters obtained in [71] and electrolyte-electrolyte pair interaction parameters set to zero; and e-NRTL BIN + EPairs is the estimation done by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature. Two equilibrium solid phases were considered: LiCl•H₂O and Li₂SO₄•H₂O.

systems with proper values of the binary interaction parameters, without considering the higher order interactions foreseen in the original e-NRTL model.

4. Conclusions

The main objective of the current work was to use the refined binary electrolyte-solvent interaction parameters of the e-NRTL model for the prediction of L-S equilibria of several systems reported in the literature.

Table 3

Prediction of the invariant points for all the ternary systems considered in this study by using the e-NRTL BIN property model.

System	T, K	Invariant points		Ref.
		Experimental	Prediction	
NaCl+KCl+H ₂ O	298.15	NaCl: 5.244 mol/kg	NaCl: 5.244 mol/kg	[79]
NaCl+SrCl ₂ +H ₂ O	288.15	KCl: 2.479 mol/kg	KCl: 2.479 mol/kg	[15]
		NaCl: 2.636 mol/kg	NaCl: 2.507 mol/kg	
KCl+SrCl ₂ +H ₂ O	288.15	SrCl ₂ : 2.477 mol/kg	SrCl ₂ : 2.729 mol/kg	[15]
		KCl: 1.332 mol/kg	KCl: 1.190 mol/kg	
KBr+SrBr ₂ +H ₂ O	288.15	SrCl ₂ : 2.961 mol/kg	SrCl ₂ : 3.112 mol/kg	[18]
		KBr: 1.212 mol/kg	KBr: 1.329 mol/kg	
LiCl+Li ₂ SO ₄ +H ₂ O	288.15	SrBr ₂ : 4.101 mol/kg	SrBr ₂ : 4.308 mol/kg	[24]
		LiCl: 18.561 mol/kg	LiCl: 18.631 mol/kg	
		Li ₂ SO ₄ : 0.024 mol/kg	Li ₂ SO ₄ : 0 mol/kg	

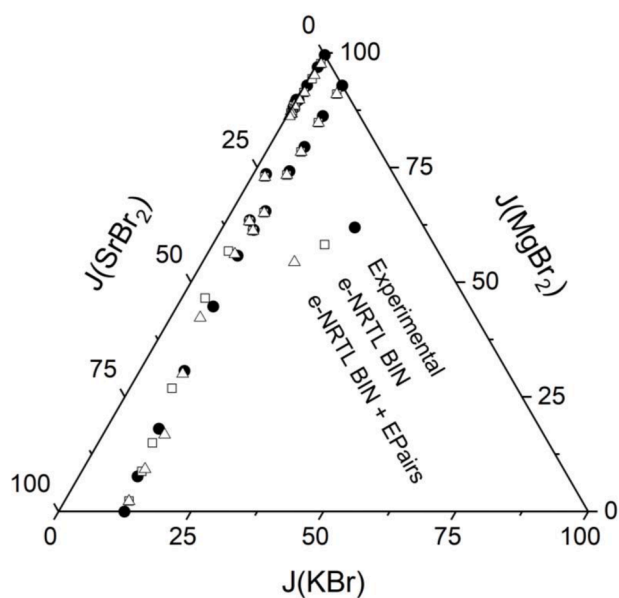


Fig. 12. Phase diagram of the quaternary system KBr+MgBr₂+SrBr₂+H₂O at 298.15 K. Experimental represents the experimental data [11]; e-NRTL BIN is the prediction made with the e-NRTL model using the refined parameters obtained in [71] and electrolyte-electrolyte pair interaction parameters set to zero; and e-NRTL BIN + EPairs is the estimation done by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature. Phase diagram is composed of four crystallization regions: KBr•MgBr₂•6H₂O, MgBr₂•6H₂O, SrBr₂•6H₂O and KBr, apart from two isothermal-isobaric invariant points and five isothermal dissolution curves [11]. The value of the solubility product of KBr•MgBr₂•6H₂O was taken from [10].

The impact on the prediction of the different equilibria is discussed when the e-NRTL parameters for estimating the electrolyte-electrolyte pairs binary interaction parameters in the prediction of the different equilibria were considered different from zero. For this purpose, experimental data from ternary and quaternary systems were fitted by non-linear regression to the complete e-NRTL model. Almost all the systems analyzed were precisely predicted by considering the e-NRTL model including the refined electrolyte-water pairs and electrolyte-electrolyte ones set to zero. However, a slight improvement of the estimations is observed for several systems when the binary electrolyte-

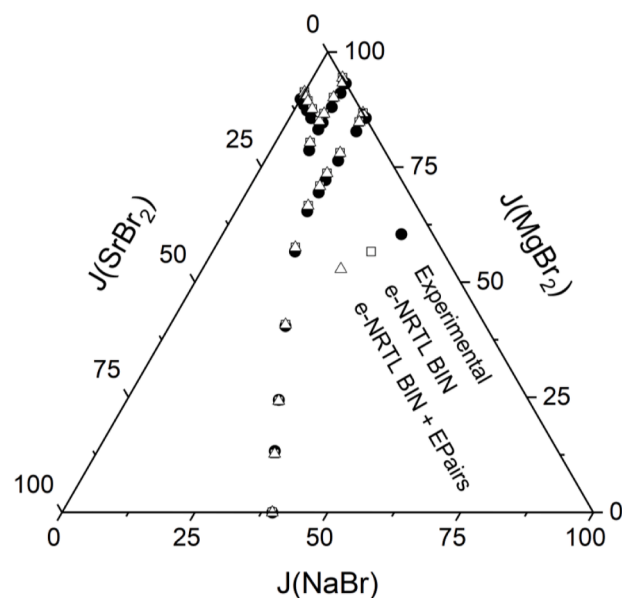


Fig. 13. Phase diagram of the quaternary system NaBr+MgBr₂+SrBr₂+H₂O at 298.15 K. Experimental represents the experimental data [11]; e-NRTL BIN is the prediction made with the e-NRTL model using the refined parameters obtained in [71] and electrolyte-electrolyte pair interaction parameters set to zero; and e-NRTL BIN + EPairs is the estimation carried out by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature. Phase diagram is composed of four crystallization regions: SrBr₂•6H₂O, NaBr, NaBr•2H₂O and MgBr₂•6H₂O. Also, there are two isothermal isobaric invariant points and five isothermal dissolution curves. The value of the solubility product of NaBr was evaluated from the solubility of the single electrolyte.

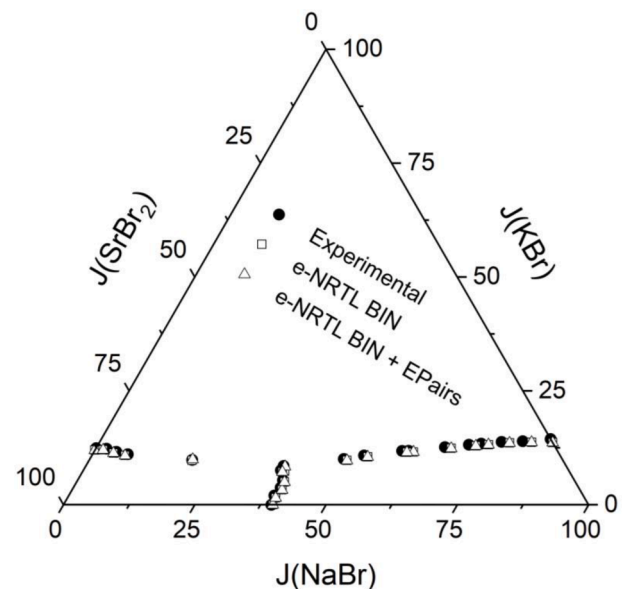


Fig. 14. Phase diagram of the quaternary system NaBr+KBr+SrBr₂+H₂O at 298.15 K. Experimental represents the experimental data [11]; e-NRTL BIN is the prediction made with the e-NRTL model but using the refined parameters obtained in [71] and electrolyte-electrolyte pair interaction parameters set to zero; and e-NRTL BIN + EPairs is the estimation done by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature. Phase diagram is composed of three crystallization regions: SrBr₂•6H₂O, KBr and NaBr•2H₂O. Also, there are one isothermal isobaric invariant point, and three isothermal dissolution curves.

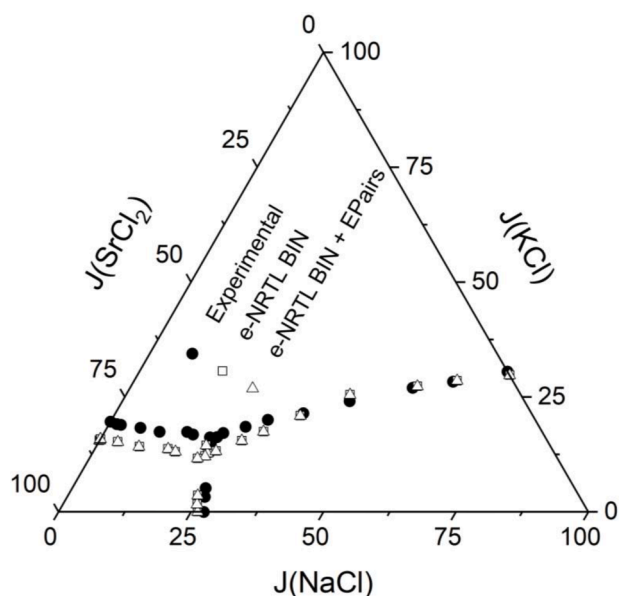


Fig. 15. Phase diagram of the quaternary system $\text{NaCl}+\text{KCl}+\text{SrCl}_2+\text{H}_2\text{O}$ at 288.15 K. Experimental represents the experimental data [2]; e-NRTL BIN is the prediction made with the e-NRTL model but using the refined parameters obtained in [71] and electrolyte-electrolyte pair interaction parameters set to zero; and e-NRTL BIN + EPairs is the estimation done by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature. Phase diagram is composed of three crystallization regions: NaCl, KCl, and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$.

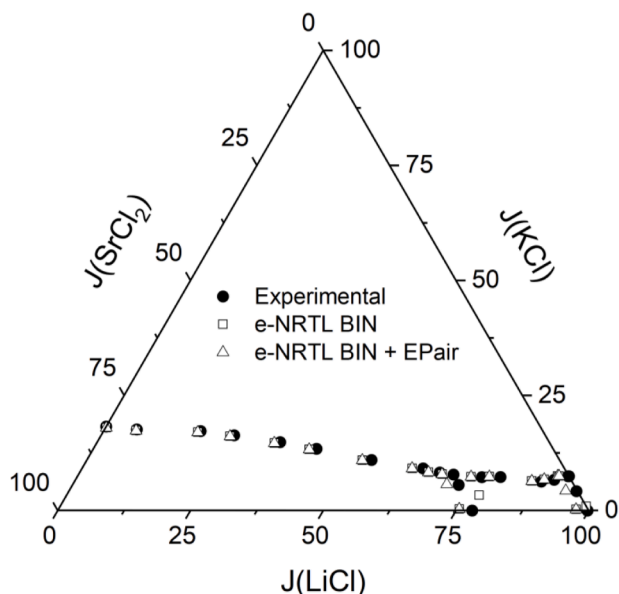


Fig. 16. Phase diagram of the quaternary system $\text{LiCl}+\text{KCl}+\text{SrCl}_2+\text{H}_2\text{O}$ at 298.15 K. Experimental represents the experimental data [10]; e-NRTL BIN is the prediction made with the e-NRTL model but using the refined parameters obtained in [71] and electrolyte-electrolyte pair interaction parameters set to zero; and e-NRTL BIN + EPairs is the estimation done by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature. Phase diagram is composed by four crystallization regions: $\text{LiCl} \cdot \text{H}_2\text{O}$, KCl, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$.

electrolyte parameters are included. Outstandingly, the $\text{Na}_2\text{SO}_4+\text{K}_2\text{SO}_4+\text{Li}_2\text{SO}_4+\text{H}_2\text{O}$ system was not properly predicted which was mainly associated to the complexity of the system considered. These results

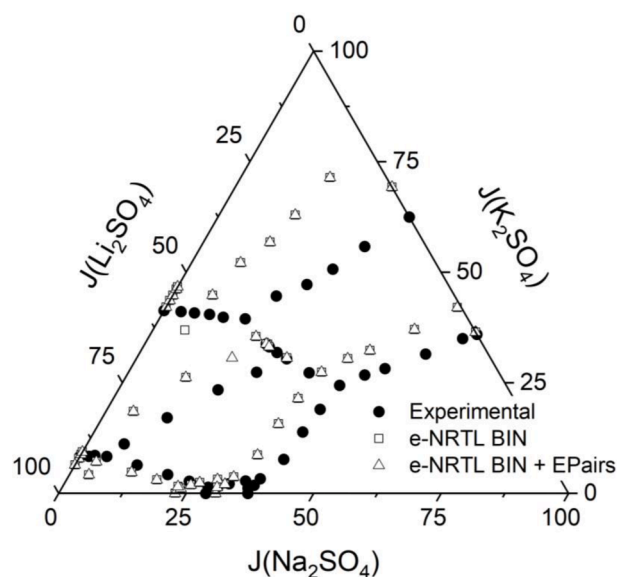


Fig. 17. Phase diagram of the quaternary system $\text{Na}_2\text{SO}_4+\text{K}_2\text{SO}_4+\text{Li}_2\text{SO}_4+\text{H}_2\text{O}$ at 288.15 K. Experimental represents the experimental data [22]; e-NRTL BIN is the prediction made with the e-NRTL model but using the refined parameters obtained in [71] and electrolyte-electrolyte pair interaction parameters set to zero; and e-NRTL BIN + EPairs is the estimation done by setting the former in the values reported, and considering the latter computed by non-linear regression of the experimental data reported in the literature. Phase diagram is composed of seven crystallization regions: three simple salts ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, K_2SO_4) and four multiple salts ($\text{Li}_2\text{SO}_4 \cdot 3\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$, $2\text{Li}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$). Also includes six isothermal-isobaric invariant points and twelve isothermal dissolution curves. The value of the solubility products of $\text{Li}_2\text{SO}_4 \cdot 3\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$, and $2\text{Li}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ were taken from literature.

would demonstrate that is possible to predict the equilibria of electrolyte systems with proper values of the binary interaction parameters, without considering the higher order interactions foreseen in the original e-NRTL model.

Author Statement

Authors affirm that this is an original work, which has not been published elsewhere and is not under consideration for publication. All the authors approve the content of this work.

Declaration of Competing Interest

The authors declare that they have not known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.fluid.2023.113832](https://doi.org/10.1016/j.fluid.2023.113832).

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