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ANALYSIS AND EXTENSION OF THE FURTER EQUATION, AND ITS APPLICATION IN THE SIMULATION OF SALINE EXTRACTIVE DISTILLATION COLUMNS

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Abstract – Simulation of saline extractive distillation columns is a difficult task owing to the high nonlinearity of the rigorous models that represent these systems. The use of simple models to obtain initial estimates of equilibrium compositions may improve the stability and rate of convergence. One of the simplest models to study the vapor-liquid equilibrium of binary liquid mixtures + salt systems is the Furter equation. This model was analyzed in the present work by means of the incorporation of activity coefficient models in the ratio of relative volatility. This approach allowed systematic extensions of the Furter equation and a brief review of the theoretical basis of the original equation. As a result of these extensions, two simple equations were proposed and tested with experimental data from 20 systems, including binary liquid mixtures + salt systems and binary liquid mixtures + ionic liquid systems. Finally, one of these proposed equations was incorporated into the GKTM software in order to assess the utility of these simple models in the simulation of saline extractive distillation columns. The obtained results showed a significant improvement over the previous algorithm.

Keywords: Electrolyte; Salt effect; Furter equation; Regular solution; Solvation; Extractive Distillation; Simulation

INTRODUCTION

Distillation is one of the most important unit operations in chemical engineering, owing to its frequent use in separation processes and the cost associated with them in the chemical industry (Gmehling, 2009). Sometimes, the separation of liquid mixtures through distillation is hindered by the existence of an azeotropic point. As is well known, conventional distillations are not able to purify binary liquid mixtures beyond the concentration of this azeotropic point. Nonetheless, distillation of mixtures that present an azeotropic point can be improved by using a separating agent, sometimes called an *entrainer* (Kiss & Suszwalak, 2012; Matsuda et al., 2011; Bastos et al., 2015; Zhang et al., 2015). The entrainer is added in order to change the volatility of the components, and depending on its effects on the mixture, it leads mainly to two different distillations: azeotropic or extractive distillation. In the first case, the entrainer induces minimum-boiling azeotropes and liquid-liquid immiscibilities to modify

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*To whom correspondence should be addressed the behavior of the mixture and allow the distillation. In the second case, the entrainer is a relatively non-volatile component that allows the distillation by shifting or even eliminating the binary azeotrope, as a result of its differential affinity with the components of the original binary liquid mixture. In comparison with azeotropic distillation, extractive distillation is simpler, can use more entrainers, and is less expensive than azeotropic distillation (Tassios, 1972). The use of high-boiling point solvents or non-volatile components in extractive distillations leads to lower energy consumptions in comparison to azeotropic distillation, because the entrainer does not need to be vaporized (Kiss & Suszwalak, 2012). In addition, the third component added in extractive distillations is often safer than the organic solvents commonly used in azeotropic distillation; this is the case, for example, of saline extractive distillations, where the entrainer is a salt, which presents very low toxicity and flammability. Although not as safe as inorganic salts as a consequence of a higher toxicity, the use of ionic liquids has recently become an interesting alternative as entrainer in SED because of their recognized advantages: in addition to their low vapor pressure, which allows an efficient recovery, ionic liquids are less corrosive and have higher solubility than inorganic salts (Bastos et al., 2015; Calvar *et al.*, 2007; Pereiro *et al.*, 2012; Vicent Orchillés *et al.*, 2008; Vicent Orchillés *et al.*, 2011, Zhang et al., 2015).

The addition of small quantities of dissolved salts or ionic liquids (Pereiro *et al.*, 2012) can shift or even eliminate the presence of the azeotropic point, thus making it possible to obtain high purity products from the top of the distillation column. The effect of the separating agent on the mixed solvent equilibrium is known as the *salt effect.* This salt effect of dissolved salts on liquid mixtures had already been studied and reported at the end of the nineteenth century (Kablukov, 1891; Miller, 1897) , then followed by systematic investigations on the subject from the 1950's (Cardoso and O'Connell, 1987; Jaques and Furter, 1974; Loehe and Donohue, 1997; Robinson and Stokes, 1959). The appearance of new materials that better withstand the highly corrosive medium associated with salt systems, the fact that the addition of salts to azeotropic mixtures avoids the requirement of a third solvent, which is usually harmful to the environment, and the increasing necessity of processes with low energy consumption, leads to a renewed interest in saline extractive distillation (SED). In this direction, several papers (Llano-Restrepo and Aguilar-Arias, 2003; Muzzio and Timmermann, 2014; Pinto *et al.*, 2000) have been recently published in order to better understand and optimize the SED process through the use of computer simulators. Computer simulation arose as one of the principal tools to improve the knowledge of the SED process, but this tool requires reliable models that allow the calculation of the phase equilibrium behavior of the system to be separated.

Several models were published as part of the aforementioned investigations, e.g., E-NRTL (Chen and Song, 2004; Mock *et al.*, 1986), LiQUAC-E (Li *et al.*, 1994; Mohs and Gmehling, 2013) and the Extended UNIQUAC (Iliuta et al., 2000; Sander *et al.*, 1986). These models are capable of very accurate VLE data regression by considering the Gibbs energy as the combination of three different range contributions: long-range, middle-range and short-range. Since some contributions are mainly theoretical (for example Debye-Hückel) and other ones are semi-empirical, with several parameters that have to be regressed from VLE data, these are limited to the range, quantity and precision of the correlated data; any extrapolation may lead to significant deviations and should be avoided. In addition, the regression of parameters is not always clear (Muzzio and Timmermann, 2014) and, often, the parameter values required for a proper data regression lack physical meaning.

On the other hand, a very useful and simple relationship was proposed by Johnson and Furter (1960):

$$\ln(\alpha_s/\alpha_0) = k.x_3 \tag{1}$$

This equation relates the ratio of relative volatilities with (α_s) and without (α_0) salt present to the salt concentration in the liquid phase (x_3). Owing to its simplicity and capacity to correlate experimental data, this model has been studied and extended by different authors (Hashitani and Hirata, 1969; Wu *et al.*, 1999; Wu *et al.*, 2001). In spite of not having a deep thermodynamic basis, the fact that only one constant is needed for a binary liquid mixture + solute system gives this equation an advantage over other semi-empirical methods like E-NRTL, which requires the regression of nine parameters for a binary liquid mixture + salt system. Nevertheless, as stated by Meranda and Furter (1971), the value of k is not expected to remain constant when the solvent compositions are varied owing to the interactions between the different components in the liquid phase (including volatile and nonvolatile). Understanding this limitation in the Furter equation, Hashitani and Hirata (1969) reported an empirical model which takes into account these interactions within the salt system, related not only to the electrolyte composition but also to the proportion of components in the binary liquid mixture:

$$\ln(\alpha_s/\alpha_0) = k_1 k_2^{z_+}.\frac{x_3}{1-x_3} \tag{2}$$

where z_+ is the mole fraction of the more volatile component in the liquid phase (salt free basis).

The current interest in extending the Furter equation throughout the entire composition range of the two volatile components leads to more recent developments (Wu *et al.*, 1999; Wu *et al.*, 2001). For example, the interesting model proposed by Wu et al. (1999) includes a quadratic term and a second constant, i.e.:

$$\ln(\alpha_s/\alpha_0) = k_1.x_3 + k_2.x_3^2 \tag{3}$$

The additional term improves the correlation of the model, as expected. Surprisingly, the proposed model does not include a term related to the proportion of the components in the binary liquid mixture.

In the present work, the Furter equation was analyzed from the consideration of activity models in the ratio of solvent volatilities. The analysis not only increased the knowledge on the Furter equation, but also set a basis for systematic extensions of this model. As a result of this approach, two new extensions of the Furter equation were proposed. One of these extensions was incorporated into a SED column simulator (GKTM, Muzzio and Timmermann, 2014) in order to improve the stability and rate of convergence of the previous algorithm, by obtaining better initial estimates of the vapor compositions at each stage. The simulation results proved that the inclusion of Furter extended models into the simulator software led to a more efficient algorithm.

FURTER EQUATION ANALYSIS

The expressions of fugacity and relative volatility of the volatile components in a binary liquid mixture + salt systems can be combined as following:

$$P\hat{\phi}_i y_i = f_i^o \gamma_i x_i \tag{4}$$

$$y_i = \frac{f_i^o \gamma_i x_i}{P\hat{\phi}_i} \tag{5}$$

The ratio of relative volatilities (binary mixture and binary mixture-salt systems) is defined as:

$$\frac{\alpha_s}{\alpha_0} = \left(\frac{y_{1,s}}{z_{1,s}}\frac{z_{2,s}}{y_{2,s}}\right) \Big/ \left(\frac{y_{1,0}}{x_{1,0}}\frac{x_{2,0}}{y_{2,0}}\right) = \frac{y_{1,s}}{y_{1,0}}\frac{y_{2,0}}{y_{2,s}} \tag{6}$$

where z_i is the mole fraction of component *i* on a salt-free basis.

At moderate pressures, Eq. (5) can be simplified with negligible error considering an ideal gas in the vapour phase and replacing the fugacity of pure liquid by the vapour pressure of the pure liquid at the considered temperature:

$$y_i = \frac{P_i^o \gamma_i x_i}{P} \tag{7}$$

Replacing in (6):

$$\begin{aligned}\frac{\alpha_s}{\alpha_0} &= \frac{\gamma_{1,s}\gamma_{2,0}x_{1,s}x_{2,0}}{\gamma_{1,0}\gamma_{2,s}x_{2,s}x_{1,0}}\frac{P_1^o(T_s)P_2^o(T)}{P_2^o(T_s)P_1^o(T)} = \\ &= \frac{\gamma_{1,s}\gamma_{2,0}}{\gamma_{1,0}\gamma_{2,s}}\frac{P_1^o(T_s)P_2^o(T)}{P_2^o(T_s)P_1^o(T)}\end{aligned} \tag{8}$$

If the temperature variation in the system after adding the salt is low enough, or if the relationships between pressures for both volatile components after adding the salt are similar, the effect related with vapour pressures of the pure liquids can be neglected in comparison to the effect related with activity coefficients. As a result, the Furter equation may be expressed as:

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = \ln\left(\frac{\gamma_{1,s}\gamma_{2,0}}{\gamma_{1,0}\gamma_{2,s}}\right) \tag{9}$$

It is convenient to introduce some additional useful definitions:

$$z_1 \equiv \frac{n_1^L}{n_1^L + n_2^L} = 1 - z_2 = \frac{x_1}{1 - x_3} \tag{10}$$

$$z_3 \equiv \frac{n_3^L}{n_1^L + n_2^L} = \frac{x_3}{1 - x_3} \tag{11}$$

$$y_1 = \frac{n_1^V}{n_1^V + n_2^V} = 1 - y_2 \tag{12}$$

$$\beta = \frac{1}{1 + z_3} \tag{13}$$

$$x_i = \beta.z_i \tag{14}$$

where z_1 and z_3 are the mole fractions of component 1 and salt respectively, on a salt free basis. The usual mole fractions of component 1 and salt are designed x_1 and $x_{3,}$ respectively.

Regular solution model

The simplest expression for the activity coefficient is the regular solution model. For the components in binary liquid mixtures, the expressions are the following (Prigogine and Defay, 1954):

$$\ln(\gamma_{1,0}) = x_{2,0}^2.A_{12} = z_2^2.A_{12} \tag{15a}$$

$$\ln(\gamma_{2,0}) = x_{1,0}^2.A_{21} = z_1^2.A_{21} \tag{15b}$$

For ternary mixtures (two volatile components and a salt), if the electrolyte is regarded as a solute, the regular solution model can be expressed as:

$$\ln(\gamma_{1,s}) = x_{2,s}^2.A_{12} + x_{3,s}^2.A_{13} + + x_{2,s}.x_{3,s}.(A_{12} + A_{13} - A_{23}) \tag{16a}$$

$$\ln(\gamma_{2,s}) = x_{1,s}^2.A_{21} + x_{3,s}^2.A_{23} + + x_{1,s}.x_{3,s}.(A_{21} + A_{23} - A_{13}) \tag{16b}$$

$$\ln(\gamma_{1,s}) = \beta^2[z_2^2.A + z_3^2.A_{13} + + z_2.z_3.(A + \Delta A)] \tag{17a}$$

$$\ln(\gamma_{2,s}) = \beta^2[z_1^2.A + z_3^2.A_{23} + + z_1.z_3.(A - \Delta A)] \tag{17b}$$

where $A \equiv A_{12} = A_{21}$; $\Delta A \equiv A_{13} - A_{23}$, the subscripts 1 and 2 are reserved for the volatile components, and the subscript 3 for the salt.

Then, Eq. (15a) and (15b) can be related by:

$$\ln\left(\frac{\gamma_{1,0}}{\gamma_{2,0}}\right) = (1 - 2.z_1).A \tag{18}$$

Similarly, Eq. (17a) and (17b) can be related by:

$$\ln\left(\frac{\gamma_{1,s}}{\gamma_{2,s}}\right) = \beta^2\{[z_2^2.A + z_3^2.A_{13} + + z_2.z_3.(A + \Delta A)] - [z_1^2.A + z_3^2.A_{23} + + z_1.z_3.(A - \Delta A)]\} = = \beta^2\ [(1 - 2.z_1).A + (1 - 2.z_1).z_3A + + z_3^2.\Delta A + z_3\Delta A] = \beta[A.(1 - 2.z_1) + z_3\Delta A] \tag{19}$$

Finally, by considering equations (6-19), and expressing the logarithm of the ratio of relative volatilities with and without salt present, the following expressions can be derived:

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = \ln\left(\frac{\gamma_{1,s}\gamma_{2,0}}{\gamma_{1,0}\gamma_{2,s}}\right) = \beta[A.(1 - 2.z_1) + + z_3\Delta A] - (1 - 2.z_1).A \tag{20}$$

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = (\beta - 1)A.(1 - 2.z_1) + x_3\Delta A \tag{21}$$

From Eq. (13), β may be approximated by 1 when z_3 is low enough and, as a consequence, Eq. (21) can be reduced to the usual Furter expression, where $k = \Delta A$. Nonetheless, if this approximation is not considered, and taking into account that $(\beta - 1) = -z_3\beta$, the salt parameter can be expressed from Eq. (21) as

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = [-(1 - 2.z_1)A + \Delta A].x_3 = k.x_3 \tag{22}$$

Equation (22) shows the functionality of the parameter with the composition of the volatile components. A more useful expression of Eq. (21) and Eq. (22) is the Furter-Regular Solution (FRS) equation

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = (\Delta A - A).x_3 + \left(\frac{2A}{\beta}\right)x_1.x_3 = = k.x_3 + k'.x_1x_3 \tag{23}$$

where β has been considered constant, since it is mostly between 0.9 and 1.

In comparison with the model proposed in Wu's work (Wu *et al.*, 1999), Eq. (23) includes a term of interaction between solvent and solute that could explain its better capacity of regression.

Solvation model

More accurate models can be introduced in Eq. (9). If the excess Gibbs energy is calculated as the sum of long-range (LR) and short-range (SR) contributions,

$$G^{E} = G^{E,LR} + G^{E,SR} \tag{24}$$

the expression for calculation of the activity coefficient of solvent *i* is:

$$\ln(\gamma_i) = \ln\left(\gamma_i^{LR}\right) + \ln\left(\gamma_i^{SR}\right) = \ln\left(\gamma_i^{LR}\gamma_i^{SR}\right) \tag{25}$$

In this approach, the long-range contribution is related to the interactions between ions, while the short-range (SR) contribution is related to interactions between all the species. Therefore, in a mixture without ions, only the short-range contribution should be considered. Replacing Eq. (25) in Eq. (9), the following equation is obtained:

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = \ln\left(\frac{\gamma_{1,s}\gamma_{2,0}}{\gamma_{1,0}\gamma_{2,s}}\right) = \ln\left(\frac{\gamma_{1,s}^{LR}\gamma_{1,s}^{SR}\gamma_{2,0}^{SR}}{\gamma_{2,s}^{LR}\gamma_{2,s}^{SR}\gamma_{1,0}^{SR}}\right) \tag{26}$$

In this equation, $y_{i,0}$ was replaced with $y_{i,0}^{SR}$ because there are no ions in the system.

The Debye-Hückel (DH) model is considered to take into account the long-range (LR) contribution in mixed solvent systems. If the partial molar volume of the solvent in the solution is approximated as the molar volume of the pure solvent, the LR logarithm can be expressed as (Li *et al.*, 1994)

$$\ln\left(\gamma_i^{LR}\right) = \left(2AM_i d/b^3 d_i\right)\left[1 + bI^{1/2} - \right. \\ \left. - \left(1 + bI^{1/2}\right)^{-1} - 2\ln\left(1 + bI^{1/2}\right)\right] \tag{27}$$

where M_i is the molecular weight of the solvent, *di* is the molar density of the pure solvent *i*, *d* is the mixed-solvent molar density; *I*, *A* and *b* are DH parameters, where $I = 0.5\,\Sigma_i m_i z_i^2$, m_i is the molality of ion *i*, v_i is the salt stoichiometric number, $A = 1.3278.10^5\ d^{0.5}/(DT)^{1.5}$ and $b = 6.360.d^{0.5}/(DT)^{0.5}$.

Nevertheless, if the DH expression is considered to have negligible effect on the phase equilibrium behaviour, as stated by Chen and Evans (1986), especially in systems with high salt concentration (m>0.1), Eq. (26) can be simplified to:

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = \ln\left(\frac{\gamma_{1,s}\gamma_{2,0}}{\gamma_{1,0}\gamma_{2,s}}\right) = \ln\left(\frac{\gamma_{1,s}^{SR}\gamma_{2,0}^{SR}}{\gamma_{2,s}^{SR}\gamma_{1,0}^{SR}}\right) \tag{28}$$

As a result, the objective is to find the effect of the salt on the activity coefficient of each solvent for the SR contribution. An interesting approach to consider in Eq. (28) is related to the solvation of ions, in which the effect of the salt is taken into account from the decrease of free solvent molecules by the solvated molecules (Robinson and Stokes, 1959). In this approach, the number of moles ($n_{i,F}$) of free solvent *i* is given by:

$$n_{i,F} = n_i - h_i n_3 \tag{29}$$

and the mole fraction ($x_{i,F}$) of free solvent *i* can be expressed as:

$$x_{i,F} = \frac{n_i - \sum_i h_i n_3}{\sum_j n_j + \left(\nu_3 - \sum_j h_j\right)n_3} = \\ = \frac{z_i - \sum_i h_i z_3}{1 + \left(\nu_3 - \sum_j h_j\right)z_3};\ j = 1,2 \tag{30}$$

wherein h_i is the solvation number of the salt with pure component of the mixed solvent system *i* and n_3 is the number of moles of salt. For binary liquid mixtures + salt systems, Eq. (30) yields:

$$x_{i,F} = \frac{z_1 - (h_1 + h_2)z_3}{1 + (\nu_3 - h_1 - h_2)z_3} \tag{31}$$

For the resolution of this solvation model, the following general thermodynamic rule is applied (Nothnagel *et al.*, 1973; Prigogine and Defay, 1954). At equilibrium, when a fluid exists in several associated forms, the chemical potential ($\mu_{i,F}$) of the monomer (free) molecule is equal to the stoichiometric (or apparent) chemical potential ($\mu_{i,}$),

$$\mu_i = \mu_{i,F}$$

In the case under study, the chemical potential of the free solvent molecule is equal to the chemical potential of solvent on a stoichiometric basis, an expression which yields:

$$\mathrm{RT}\ln(\gamma_i x_i) = \mathrm{RT}\ln(\gamma_{i,F}\, x_{i,F}) \tag{32}$$

$$\gamma_i = \frac{x_{i,F}}{x_i}\gamma_{i,F} \tag{33}$$

If the free solvent non-ideality is considered to be only due to electrostatic forces (DH) with ions and the interaction with the other solvent, then the activity coefficient can be rearranged from Eq. (33) as

$$\ln(\gamma_i) = \ln\left(\frac{x_{i,F}}{x_i}\right) + \ln(\gamma_{i,0}^{SR}) + \ln(\gamma_i^{DH}) \tag{34}$$

For a binary system, Eq. (34) can be written as:

$$\ln(\gamma_1) = \ln\left[\frac{\left(1 - \frac{h_1 z_3}{z_1}\right)(1 + \nu_3 z_3)}{1 + (\nu_3 - h_1 - h_2) z_3}\right] + \tag{35}$$

$$+ \ln(\gamma_{1,0}^{SR}) + \ln(\gamma_1^{DH})$$

$$\ln(\gamma_2) = \ln\left[\frac{\left(1 - \frac{h_2 z_3}{z_2}\right)(1 + \nu_3 z_3)}{1 + (\nu_3 - h_1 - h_2) z_3}\right] + \tag{36}$$

$$+ \ln(\gamma_{2,0}^{SR}) + \ln(\gamma_2^{DH})$$

In the present work, h_i is calculated as a function of z_i, i.e., $h_i = h_i^{\infty} z_i^2$ where h_i^{∞} is the solvation number of salt with component i at infinite dilution of the salt. Replacing Eq. (34) in Eq. (28), the Furter-Solvation (FS) model is obtained:

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = \ln\left(\frac{\gamma_{1,s}^{SR}\gamma_{2,0}^{SR}}{\gamma_{2,s}^{SR}\gamma_{1,0}^{SR}}\right) = \ln\left(\frac{x_{1,F}\, x_2}{x_{2,F}\, x_1}\right) \tag{37}$$

$$\ln\left(\frac{\alpha_s}{\alpha_0}\right) = \ln[(1 - h_1^{\infty} z_1 z_3)/(1 - h_2^{\infty} z_2 z_3)] \tag{38}$$

EVALUATION OF EXTENDED MODELS

The results of applying Eq. (1), Eq. (3), Eq. (23) and Eq. (38) are reported in Table 1. Correlation of experimental data (Calvar *et al.*, 2007; Peña *et al.*, 1994; Peña *et al.*, 1995; Peña *et al.*, 1996; Vercher *et al.*, 1994; Vercher *et al.*, 1995; Vercher *et al.*, 1996a; Vercher *et al.*, 1996b; Vercher *et al.*, 1999; Vercher *et al.*, 2001; Vercher *et al.*, 2002; Vercher *et al.*, 2003; Vercher *et al.*, 2004a; Vercher *et al.*, 2004b; Vercher *et al.*, 2005; Vercher *et al.*, 2006; Vicent Orchillés *et al.*, 2008; Vicent Orchillés *et al.*, 2011; Zemp and Francesconi, 1992) through the four models was carried out by seeking the parameters that minimized the objective function, defined by:

$$OF = \sum_{i=1}^{n} \left|\left(y_{1,s}^{cal} - y_{1,s}^{exp}\right)\right| / N = \Delta y_{1,s} \tag{39}$$

where N is the number of experimental points, $y^{exp}_{1,s}$ is the experimental vapour phase mole fraction, and $y^{cal}_{1,s}$ is the vapour phase mole fraction calculated from $y^{\mathrm{exp}}_{1,s} = z_1/[z_1 + (1 - z_1)/\alpha_s]$. In order to obtain the best parameters from experimental data, the Solver tool of the Microsoft Excel spreadsheet was used to minimize the objective function.

The FRS and FS models yielded better results than the original Furter equation, as was expected since the proposed equations comprise two parameters. In comparison to the two-parameter Wu model (Wu *et al.*, 1999), the FRS and FS models have a better performance in most of the analyzed systems. The average errors for every model show to what extent the models developed in this work improved the correlation of experimental data. The parameters regressed for each model are summarized in Table 2; in particular, parameters for both forms of the FRS model are informed. As can be seen, the restriction of positive values for the solvation parameters at infinite dilution (h_i^0) has been relaxed in order to obtain the best OF result (Eq. (39)). A comparison of the curves obtained from each model for the VLE data of the acetone + methanol + lithium nitrate system (Vercher *et al.*, 2006) is depicted in Fig. 1. Both the FRS and FS models yielded the better correlations.

PROCESS SIMULATION

The extended models proposed in this work can be readily incorporated in a simulator of SED columns.

Table 1. Results obtained from Furter, Wu, FRS and FS models.

System	Condition	x_3[a]	$\Delta y_{1,s}$			
			Furter[b]	**Wu**[c]	**FRS**[d]	**FS**[e]
Propanol-water-$LiNO_3$	100.0kPa	0.02-0.121	0.0151	0.0140	0.0081	0.0080
Acetic acid-water-CH_3COONa	100.0kPa	0.0038-0.1185	0.0116	0.0111	0.0094	0.0090
Propanol-water-LiCl	100.0kPa	0.021-0.126	0.0150	0.0150	0.0091	0.0094
Propanol-water-$CuCl_2$	100.0kPa	0.021-0.118	0.0120	0.0098	0.0113	0.0122
Propanol-water-$Ca(NO_3)_2$	100.0kPa	0.009-0.144	0.0188	0.0154	0.0164	0.0118
Ethanol-water-CH3COOK	101.33kPa	0.025-0.15	0.0260	0.0258	0.0217	0.0223
Acetone-methanol-$LiNO_3$	100.0kPa	0.021-0.16	0.1319	0.1250	0.0477	0.0273
Ethanol-water-[C6mim][Cl]	101.3kPa	0.002-0.325	0.0534	0.0406	0.0533	0.0342
Ethanol-water-KNO_3	100.0kPa	0.001-0.032	0.0123	0.0123	0.0104	0.0110
Ethanol-water-$NaNO_3$	100.0kPa	0.003-0.153	0.0202	0.0196	0.0188	0.0212
Ethanol-water-$CuCl_2$	100.0kPa	0.007-0.097	0.0167	0.0167	0.0166	0.0279
Ethanol-water-$CoCl_2$	100.0kPa	0.007-0.072	0.0146	0.0123	0.0142	0.0154
Ethanol-water-$SrBr_2$	100.6kPa	0.007-0.064	0.0197	0.0197	0.0162	0.0157
Ethanol-water-$SrCl_2$	100.0kPa	0.004-0.045	0.0196	0.0196	0.0194	0.0191
Ethanol-water-$SrNO_3$	100.0kPa	0.002-0.053	0.0192	0.0174	0.0160	0.0156
Acetic acid-water-CH_3COOK	100.0kPa	0.0099-0.1199	0.0162	0.0138	0.0114	0.0109
Acetic acid-water-CH_3COOLi	100.0kPa	0.021-0.127	0.0134	0.0087	0.0112	0.0108
Propanol-water-[emim][triflate]	100.0kPa	0.0533-0.3165	0.0823	0.0796	0.0343	0.0294
Propanol-water-[beim][triflate]	100.0kPa	0.0425-0.3239	0.0917	0.0904	0.0334	0.0294
Propanol-water-[bmpyr][triflate]	100.0kPa	0.0527-0.3274	0.0877	0.0867	0.0346	0.0307
Average			0.035	0.033	0.021	0.019

[a] Range of salt concentration for the selected data.
[b] Results obtained by means of Furter equation.
[c] Results obtained by means of Wu equation.
[d] Results obtained by means of Furter-Regular Solution model.
[e] Results obtained by means of Furter-Solvation model.

Table 2. Parameters of the Furter, Wu, FRS and FS models, used in the correlation of systems included in Table 1.

System	**Furter**[a]	**Wu**[b]		**FRS**[c]				**FS**[d]	
	k	k	k′	k	k′	A	ΔA	h_{10}	h_{20}
Propanol-water-$LiNO_3$	6.02	7.37	-13.67	4.23	4.33	6.40	2.17	-10.62	2.80
Acetic acid-water-CH_3COONa	0.39	-0.03	4.59	-1.41	4.47	0.83	2.24	-2.72	-1.34
Propanol-water-LiCl	7.81	7.74	0.63	6.33	4.22	8.44	2.11	-13.86	4.03
Propanol-water-$CuCl_2$	4.55	6.28	-19.69	4.04	1.32	4.70	0.66	-6.14	2.92
Propanol-water-$Ca(NO_3)_2$	10.17	13.09	-36.03	6.85	6.19	9.95	3.10	-18.61	4.16
Ethanol-water-CH_3COOK	6.03	7.64	-20.82	2.77	7.62	6.58	3.81	-11.77	1.97
Acetone-methanol-$LiNO_3$	7.03	17.29	-89.46	-7.45	43.10	14.10	21.55	-130.62	-31.84
Ethanol-water-[C6mim][Cl]	-1.68	-4.42	16.10	-2.65	2.42	-1.44	1.21	0.24	-0.41
Ethanol-water-KNO_3	9.35	9.34	0.17	13.25	-48.87	-11.19	-24.44	10.08	9.32
Ethanol-water-$NaNO_3$	7.12	5.70	13.55	7.98	-11.93	2.01	-5.96	-5.31	4.38
Ethanol-water-$CuCl_2$	5.45	5.44	0.16	5.12	1.52	5.88	0.76	5.10	4.82
Ethanol-water-$CoCl_2$	10.85	14.53	-81.85	12.71	-4.69	10.36	-2.35	-8.83	9.52
Ethanol-water-$SrBr_2$	16.79	16.77	0.60	13.91	11.38	19.60	5.69	-33.78	9.63

Table 2. Cont.

System	Furter[a]	Wu[b]		FRS[c]				FS[d]	
	k	k	k´	k	k´	A	ΔA	h_{10}	h_{20}
Ethanol-water-$SrCl_2$	17.28	17.28	-0.02	16.04	7.20	19.64	3.60	-29.44	12.01
Ethanol-water-$SrNO_3$	10.03	3.39	177.80	13.11	-31.36	-2.57	-15.68	6.77	9.27
Acetic acid-water-CH_3COOK	2.01	-1.93	48.79	-1.46	7.56	2.32	3.78	-6.00	-1.51
Acetic acid-water-CH_3COOLi	-1.69	-4.60	31.41	-3.15	3.19	-1.55	1.59	-0.04	-3.33
Propanol-water-[emim][triflate]	1.45	3.32	-8.02	-2.30	10.39	2.89	5.20	-8.99	-3.37
Propanol-water-[beim][triflate]	0.03	1.44	-5.03	-3.69	10.33	1.47	5.16	-7.34	-6.57
Propanol-water-[bmpyr][triflate]	0.48	1.49	-4.01	-3.10	9.79	1.80	4.90	-7.32	-5.15

[a] Parameters obtained for Furter equation.
[b] Parameters obtained for Wu equation.
[c] Parameters obtained for Furter-Regular Solution model.
[d] Parameters obtained for Furter-Solvation model.

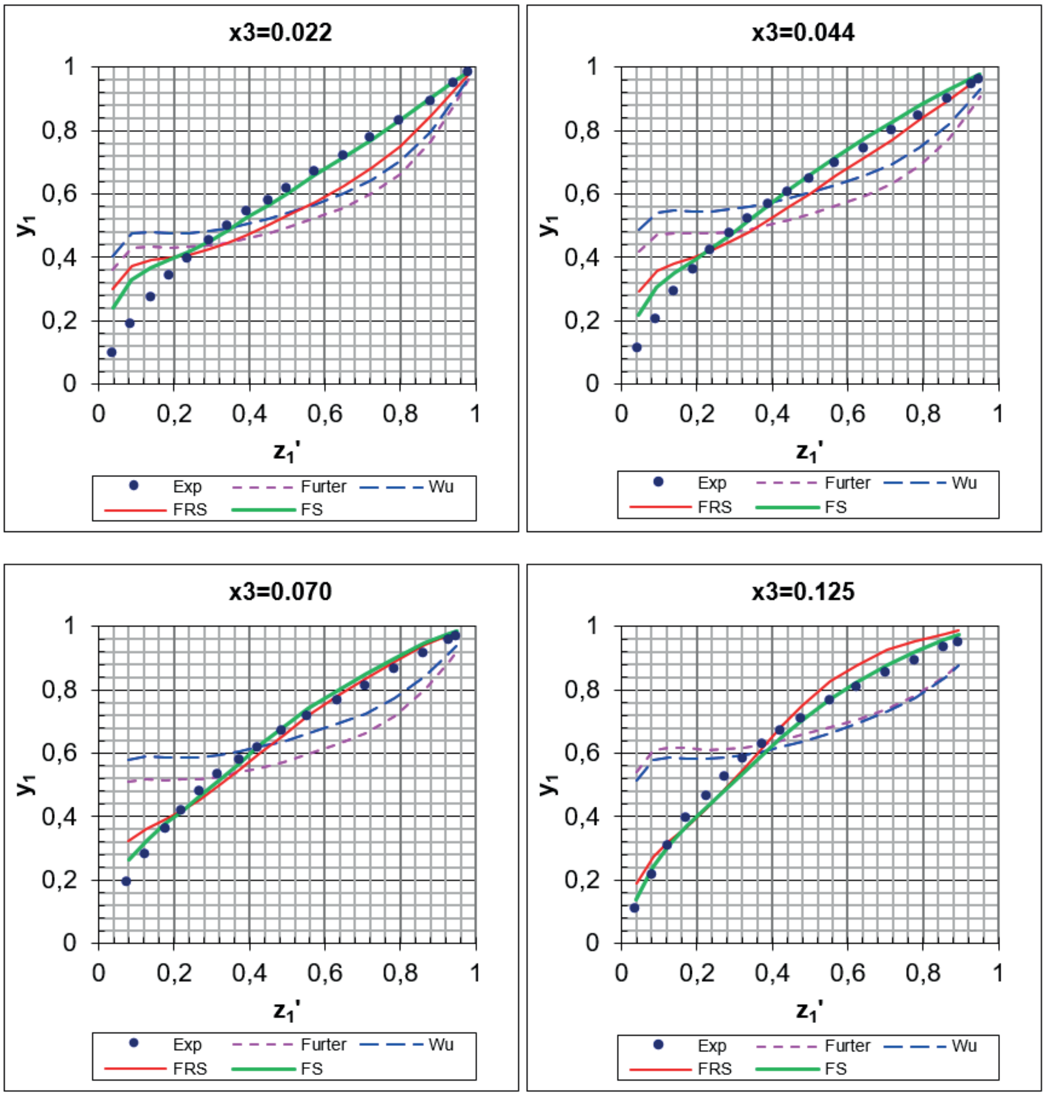

Figure 1. Isobaric z'-y diagrams for acetone + methanol + lithium nitrate system (•: experimental data obtained from Vercher et al. (2006); – – – –: calculated data using Furter equation; – – –: calculated data using Wu equation; ——: calculated data using FRS model; ——: calculated data using FS model).

Taking advantage of their mathematical simplicity, the models developed as extensions of the Furter equation can offer a good starting point for simulators based on algorithms for simultaneous resolution of nonlinear equation systems, e.g. Newton-Raphson's algorithm. As is well known, these algorithms are sensitive to the initial estimates, and a large error in the initial estimates can contribute to the convergence failure. On the other hand, as proved in a previous work (Muzzio and Timmermann, 2014), the temperature profiles of SED columns have significant differences in comparison with conventional columns, hampering the estimation of compositions from usual models where temperature is an input. Fortunately, the extended models based on the Furter equation are not limited by this requirement, thus providing initial estimates from the approximate knowledge of compositions and flows of input streams. To obtain this approximate knowledge, a SED column can be simulated as a conventional column in a first approach, i.e., a column without electrolyte. From the results of liquid and vapor flows and compositions for each stage, and the knowledge of the inlet stream of salt, an estimate of the salt composition in the liquid phase for each stage can be calculated. Then, in the Furter estimation-correction (FEC) approach, the vapor composition at each stage is corrected by means of, for example, the FRS model. These corrected compositions are the initial estimates that will be used to solve the complete non-linear equation system (Naphtali and Sandholm, 1971). The different steps of the FEC algorithm, in comparison with the stepwise heat addition (SHA) algorithm (Muzzio and Timmermann, 2014), are shown in Fig. 2. To prove the utility of the proposed approach, the FRS model was incorporated and tested in the GKTM simulator, where two systems were simulated: ethanol-water-potassium acetate, and 1-propanol-water-lithium nitrate. The properties and process conditions considered for these systems are tabulated in Table 3. The simulations carried out by using the FEC-FRS approach (Furter estimation-correction algorithm, where estimations are carried out by means of the Furter-Regular Solution model), were compared to the ones performed by the previous SHA algorithm. As can be seen from the results in Figures 3-6, the number of iterations and convergence time were significantly enhanced by using the FEC-FRS approach.

The FEC-FRS algorithm proved to be faster than the SHA algorithm, as depicted in Fig. 3. The difference is more evident when the salt values are low because the corrected estimates in the FEC-FRS algorithm are close to the final solution, thus requiring few iterations in the Newton-Raphson step (Fig. 4). The rate of convergence for the FEC-FRS algorithm is also superior when applied to systems with high condenser and reboiler duties, because the SHA algorithm requires more iterations between Newton-Raphson and heat addition steps. As can be seen from Fig. 5 and Fig. 6, the FEC-FRS is less affected than the SHA algorithm by the addition of stages in the simulated column. Finally, when the salt composition in the column stages are high, the FEC-FRS algorithm proved to be more stable than the SHA algorithm.

Table 3. Properties and process conditions for the simulated systems.

System	**1-Propanol-Water-$LiNO_3$**		**EtOH-Water-KAc**	
Algorithm	**SHA**[a]	**FEC-FRS**[b]	**SHA**[a]	**FEC-FRS**[b]
Rigorous model	E-NRTL	E-NRTL	E-NRTL	E-NRTL
Main feed - flow rate ("F")	100 kmol/h	100 kmol/h	100 kmol/h	100 kmol/h
Main feed - mole fraction ("Fx1")	0.3	0.3	0.3	0.3
Main feed - water mole fraction ("Fx2")	0.7	0.7	0.7	0.7
Main feed - temperature ("TF")	362 K	362 K	357 K	357 K
Main feed - stage	4	4	5-14	5-14
Salt feed - flow rate ("Q")	1 kmol/h	1 kmol/h	3 kmol/h	3 kmol/h
Salt feed - mole fraction ("Qx1")	0.8-0.95	0.8-0.95	0.95	0.95
Salt feed - salt mole fraction ("Fx2")	0.05-0.2	0.05-0.2	0.05	0.05
Salt feed - stage	1	1	1	1
Salt feed - temperature ("TQ")	360 K	360 K	360 K	360 K
Operating pressure ("P")	1 atm	1 atm	1 atm	1 atm
Number of equilibrium stages ("N")	7	7	7-16	7-16
Condenser duty ("Qc")	-100000 kJ/h	-100000 kJ/h	-500000 kJ/h	-500000 kJ/h
Reboiler duty ("Qr")	100000 kJ/h	100000 kJ/h	100000 kJ/h	100000 kJ/h

[a] Stepwise heat addition algorithm.

[b] Furter estimation-correction algorithm, where estimations are carried out by means of the Furter-Regular Solution model.

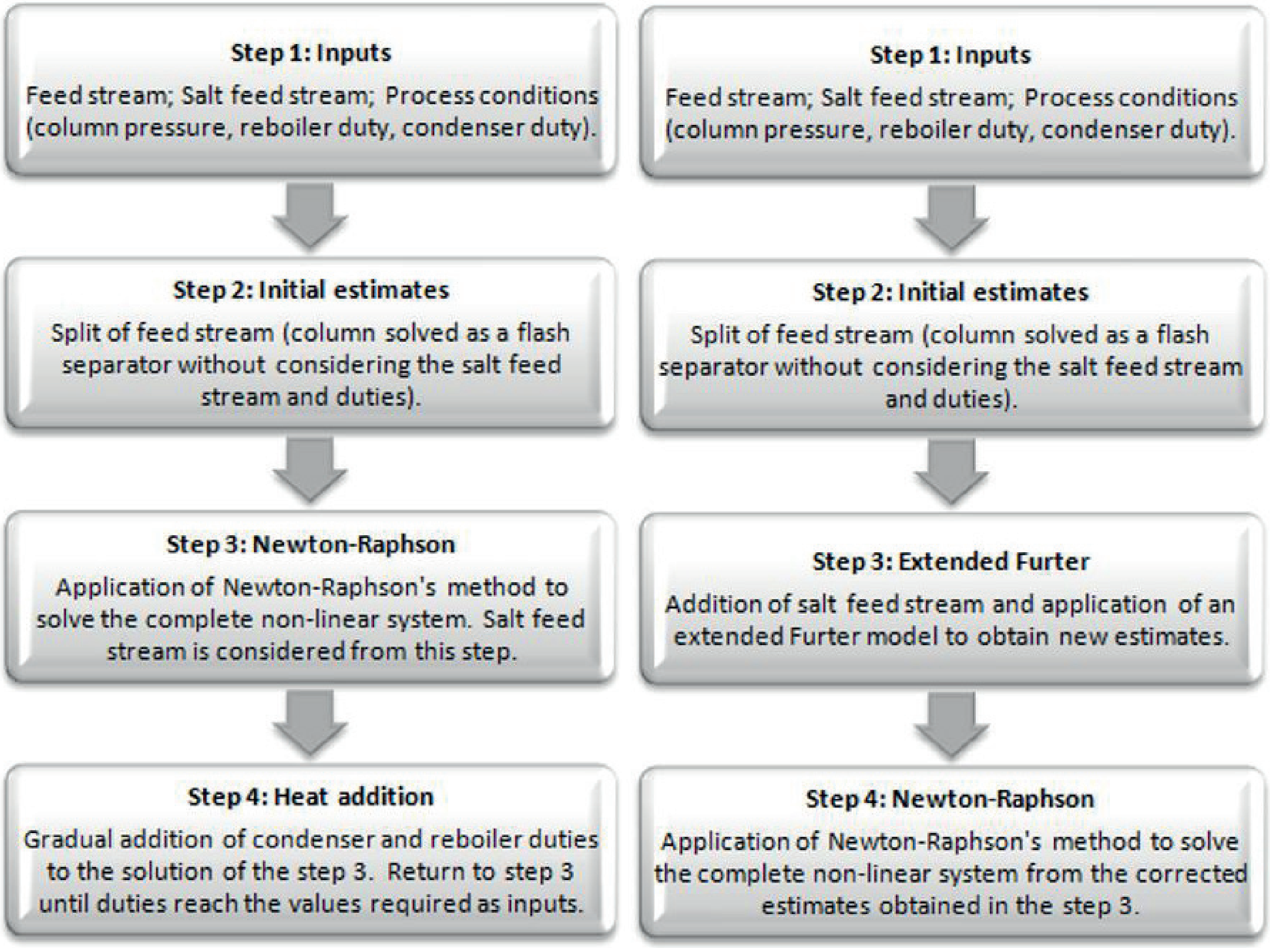

Figure 2. Comparison between the SHA (left) and FEC-FRS (right) approach.

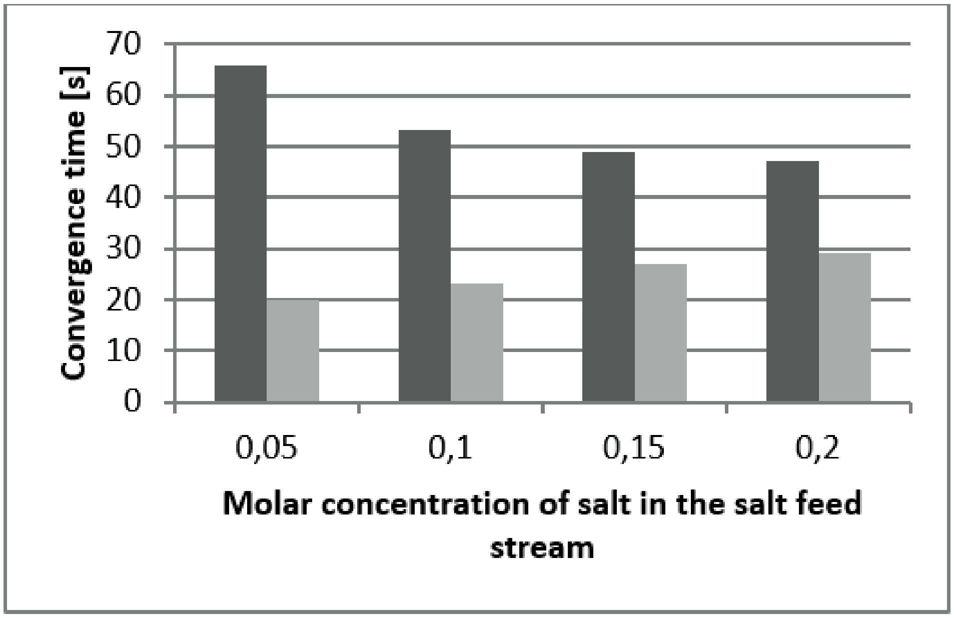

Figure 3. Comparison of convergence time for the SHA approach (dark grey columns), and the FEC-FRS approach (light grey columns). Simulated system: 1-Prop-H_2O-$LiNO_3$.

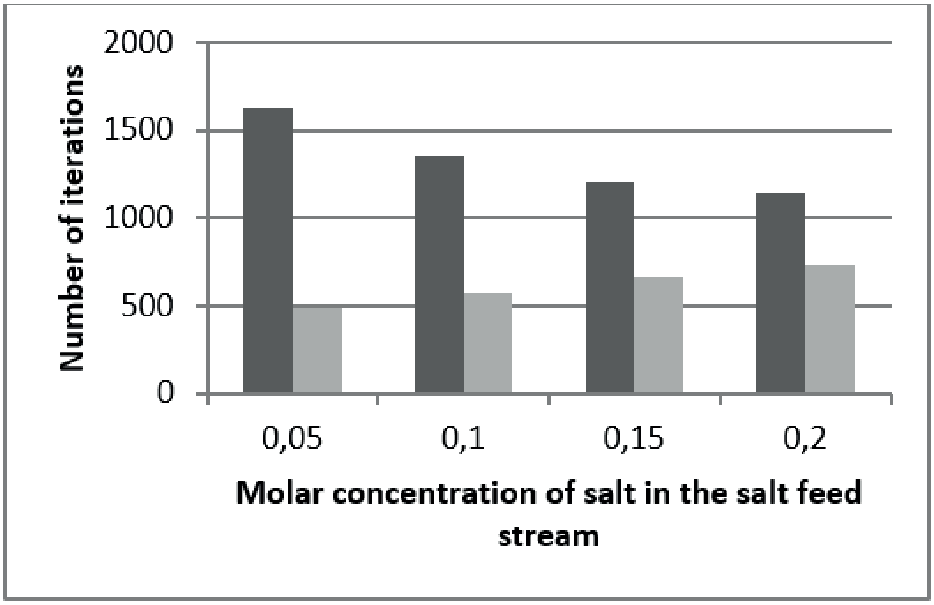

Figure 4. Comparison of the number of iterations required to achieve convergence, for the SHA approach (dark grey columns), and the FEC-FRS approach (light grey columns). Simulated system: 1-Prop-H_2O-$LiNO_3$.

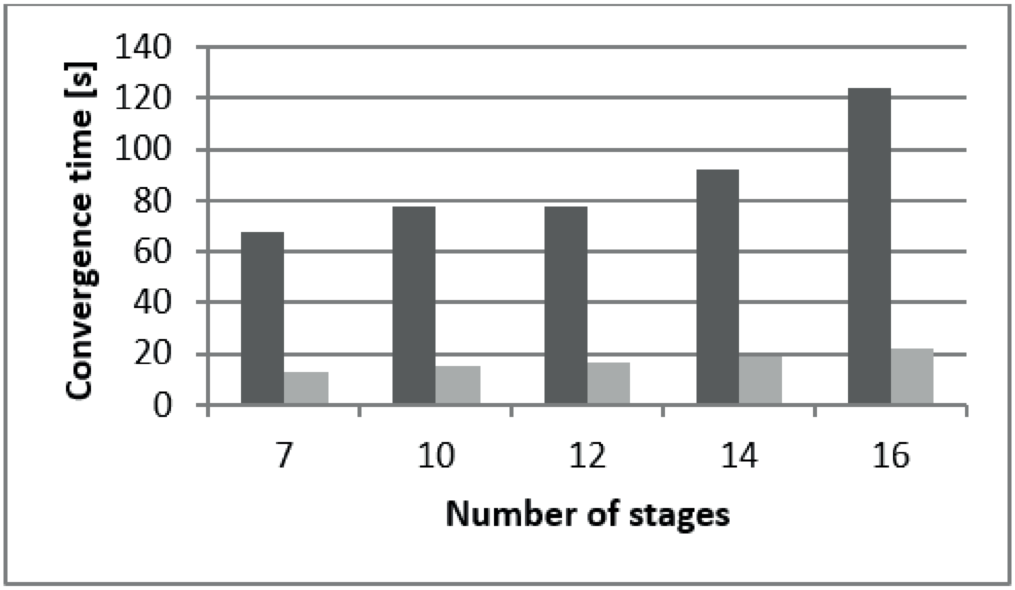

Figure 5. Comparison of convergence time for the SHA approach (dark grey columns), and the FEC-FRS approach (light grey columns). Simulated system: EtOH -H_2O-KAc.

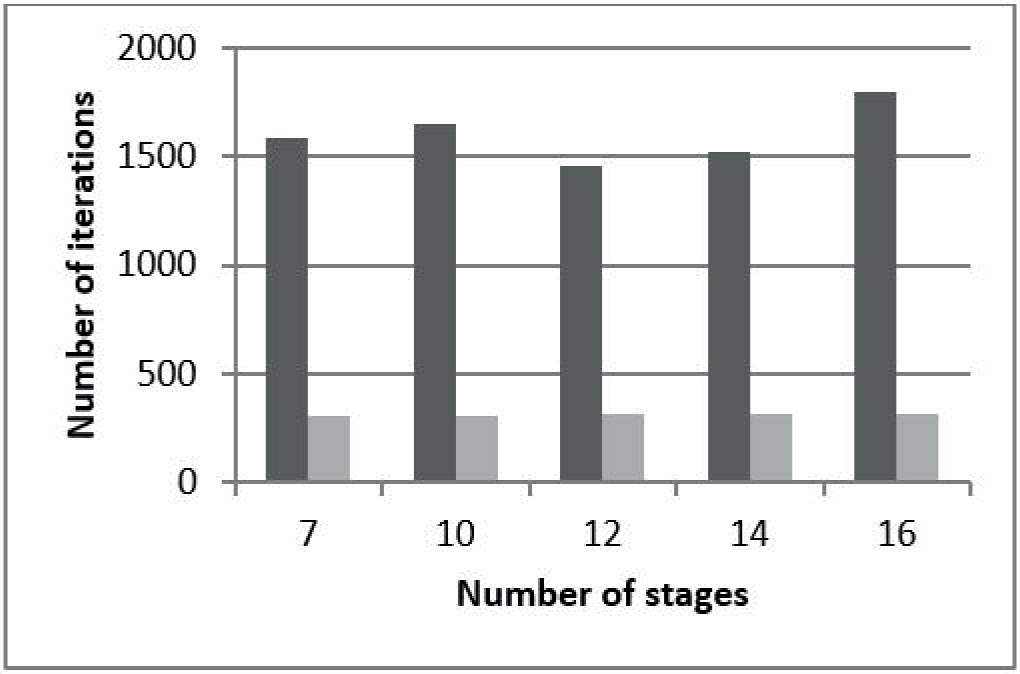

Figure 6. Comparison of the number of iterations required to achieve convergence, for the SHA addition approach (dark grey columns), and the FEC-FRS approach (light grey columns). Simulated system: EtOH -H_2O-KAc.

CONCLUSIONS

In this work, the Furter equation has been studied and extended by means of the activity models approach. As a result of this analysis, two new models have been proposed as extensions of the Furter equation. These new models retain the simplicity and improve the average deviation of vapor phase mole fraction in comparison to previous models, including another two-parameter model proposed by Wu et al. (1999), even when applied to the entire salt/solvent concentration range. In addition, through the consideration of activity coefficients, the interactions between the different components (volatile and nonvolatile) were included in the model. As a consequence, the relationship between the Furter constant and the proportion of the volatile components arose naturally.

Although the new models developed in this work are an improvement over previous equations, more important is the possibility offered by the activity coefficient approach to be used as a tool to extend the Furter equation toward even more accurate models.

Finally, the Furter extended models have been integrated into a SED column simulator in order to enhance the stability and rate of convergence. Since these models are not affected by the uncertainty in the temperature profile of the distillation column, the vapor compositions at each stage can be corrected from a conventional distillation column to a SED column. As has been proved from the simulation results of two different systems, the inclusion of Furter extended models into the simulator software led to a more efficient algorithm.

NOMENCLATURE

A_{ij} : parameter of the regular solution model.
C,C',C": constant of integration
f_i: fugacity of component *i* in the liquid phase
G^E : molar excess Gibbs free energy
h_i : solvation number of salt with component *i*.
H_i: molar enthalpy of component "i"
k, *k*': parameter of the salt effect.
n^{α}_i: number of moles *"i"* in *α* phase.
P: pressure.
R: universal constant gas.
S_i: molar entropy of component "i".
T: temperature.
V_i: molar volume of component "i".
x_i: liquid phase mole fraction of component "i" based on undissociated species.
x_{ia}: effective mole fraction of solvent "*i"* on a salt free basis.
y_i: vapor phase mol fraction of component "i" in the salt-free system.
Δy_{1s} : $\sum_{i=1}^{n}\left|\left(y_{1,s}^{cal}-y_{1,s}^{exp}\right)\right|/N$, N is the number of data points considered.

z_i : liquid phase mol fraction for component "*i*", on a salt free basis.

Greek letters

α : relative volatility

β : $1/(1+z_3)$

$\hat{\phi}_i$: fugacity coefficient of the component *i* in the mixture.

γ_i : activity coefficient for the solvent *i*

μ_i^α : chemical potencial of component "i" in the *α* phase.

μ_{ij}^α : derivative of chemical potential of component "i" with respect to "j" component in the *α* phase.

v_3 : electrolyte stoichiometric coefficient.

σ : saline coefficient.

Subscripts

F : free molecule

s : system with salt

\+ : property of the more volatile component

0 : salt-free system

1,2 : volatile components

3 : non-volatile component (salt or ionic-liquid)

Superscripts

LR : long-range.

SR : short-range.

∞ : infinite dilution of the salt

° : pure component

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