

EFFECT OF ELECTROLYTES ON THE TEMPERATURE PROFILE OF SALINE EXTRACTIVE DISTILLATION COLUMNS

C.R. MUZZIO[†] and E.O. TIMMERMAN[‡]

[†] Dto. de Química, Facultad de Ingeniería, Univ. de Buenos Aires, Paseo Colón 850, Buenos Aires, Argentina.
cmuzzio@fi.uba.ar

[‡] Instituto de Investigación y Desarrollo, Academia Nac. de Ciencias de Buenos Aires, Av. Alvear 1711, Buenos Aires, Argentina
eotimmer@yahoo.com.ar

Abstract— The effect of electrolytes in the temperature profile of saline extractive distillation columns is analyzed using a Newton–Raphson based program (acronym GKTM) with a new increase-by-step technique and applied to the system 1-propanol-water-LiNO₃. In addition, the E-NRTL model is examined in order to validate its capability of making accurate predictions of phase equilibrium behavior and its suitability for simulation of extractive distillation columns. Special aspects of the phase equilibrium of mixed solvents electrolyte systems are analyzed. These particular features determine the special temperature profile in these cases.

Keywords— Mixed solvent electrolytes; Salt effect on extractive distillation; Simulation using Newton–Raphson; E-NRTL; Phase equilibrium aspects.

I. INTRODUCTION

Saline extractive distillation (SED) is a unit operation based on the effect of salts on mixed solvent systems. When this effect is present, the distillation of solvents with similar boiling points is facilitated and the use of energy decreases. This phenomenon is of particular importance when the system is an azeotropic one, where small quantities of salt are capable of shifting, or even eliminating, the azeotrope, making it possible to get a high-purity product from the top of a column. In spite of its benefits, already known in the nineteenth century, the process of saline extractive distillation was neglected due to the complete lack of a theory that explains the thermodynamic behavior of a mixed-solvent salt system. Moreover, many authors recently studied the “salt effect” in simulated columns and the conclusions obtained were often thermo-dynamically inconsistent.

Although studies of the saline effect have already been reported at the end of the nineteenth century (Kablukov, 1891, Miller, 1897), systematic investigations on the subject began in the 1950-60, e.g. Johnson and Furter (1960), Robinson and Stokes (1959); Cook and Furter (1968), Meranda and Furter (1971), Furter (1977), Cardoso and O’Connell (1987), Loehe and Donohue (1997). Recently, the E-NRTL model was developed (Chen *et al.*, 1982, 1999, 2001; Chen and Mathias, 2002; Chen and Song, 2004; Mock *et al.*, 1986), based upon the NRTL model proposed by Renon and Prausnitz (1968), to predict and correlate the deviation from ideality in mixed-solvent salt solutions. Accurate data regressions by means of E-NRTL model have been reported recently by Vercher *et al.* (1999, 2002, 2003,

2004, 2005) and in the present work some particular aspects of the ability of E-NRTL to make accurate predictions will be discussed (see Section II.B). However, it is worth noting that, in spite of not having a deep thermodynamic basis, other current semi-empirical models are also suitable for predicting the appearance of special characteristic points of the phase equilibrium diagram of mixed-solvent electrolyte systems, the thermodynamic foundation of which are recently given (Muzzio, 2006)

In the field of simulations of extractive distillation column, Pinto *et al.* (2000) reported a comparison between SED and conventional extractive distillation, carried out with the help of a commercial simulator. According to their results, saline extractive distillation process would be better than conventional ones due to minor heat consumption and the use of non-toxic solvents. Moreover, some local minima in the temperature profile were found.

Nonetheless, Llano-Restrepo and Aguilar-Arias (2003) stated the existence of inconsistencies between experimental evidence and the results obtained by Pinto *et al.* In addition, they simulated a saline extractive distillation column through a steady-state equilibrium-stage model based on normalized MESH (material, equilibrium and energy balance) equations. However, the high concentration of salt used in that simulation eliminated the azeotrope. Furthermore, the local minima in the temperature profile found in Pinto’s work disappeared in the paper by Llano-Restrepo and Aguilar-Arias. As it will be shown, an extreme in the middle region of a SED column is a direct consequence of the phase diagram of these systems and, depending on column conditions, it must appear when the system presents an extreme of temperature due to a ‘pseudo-azeotropic’ point.

Figures 1-3 illustrate a total reflux distillation of a theoretical system with a phase diagram such as the shown in Fig. 1, which corresponds to the system 1-propanol(1)-water(2)-LiNO₃(3) ($x_3=0.06$) (Vercher *et al.* (2002)). In these figures the dashed lines represent equilibrium stages in a total reflux distillation. Even though in most of the works T-x’(salt free basis)-y diagrams are avoided, in this work these diagrams are fundamental to understand the causes of the temperature profile in a SED column. It is readily seen that in this distillation a minimum of temperature appears in the middle region of the column, at a different concentration of the pseudo-azeotrope: in Fig. 3 it can be observed that there is an extreme at 363.3 K, and this point is reached at

$x_1=0.31$, while the point that corresponds with equal composition of vapor and liquid phase (salt free basis) is placed approximately at $x_1=0.54$. The characteristics of this pseudo-azeotropic point has been studied with some detail by Sander *et al.* (1986a, 1986b) and there it has been stated that this point presents only one of the two characteristic features of the genuine azeotrope of a conventional binary azeotropic system, i.e. to have the same composition in the liquid and vapor phase, but without an extremum of temperature (or pressure). This other characteristic of a genuine azeotrope, i.e. the extremum of temperature (or pressure), is displayed by another equilibrium point much less studied and usually over looked, which presents different compositions in liquid and vapor. As mentioned previously, the existence and properties of both points has been recently thermodynamically justified (Muzzio, 2006).

Points A-B and C in Fig 1 are these special equilibrium states. The crossing point C is the actual 'pseudo-azeotropic' point, as it can be appreciated in Fig. 2, which is certainly the point of crucial importance for distillation. On the other hand, the state A-B determines the minimum in the temperature profile, but, besides this, it is not relevant for the distillation process (in Fig. 2 this point lays off the diagonal). Moreover, point D does not correspond to coexisting liquid and vapor phases, as already stated Sander *et al.* (1986a, 1986b).

The thermodynamic foundation for the appearance of these points in these systems instead of a normal azeotropic state is very simple. A normal azeotropic state is an indifferent state, a state at which phase reactions occur without composition changes in the involved phases. And it is because of this condition that a normal azeotropic point presents a typical behavior of a VL-equilibrium of a pure substance and is also characterized by a simple T-P relation of the Clausius-Clapeyron type (Saurel's theorem, 1899; see Prigogine and Defay, 1954).

On the other hand, in the presence of a non-volatile solute in the liquid phase, not necessarily an electrolyte, such an indifferent behavior is not allowed. By the evaporation of liquid solvent-mixtures the solute con-

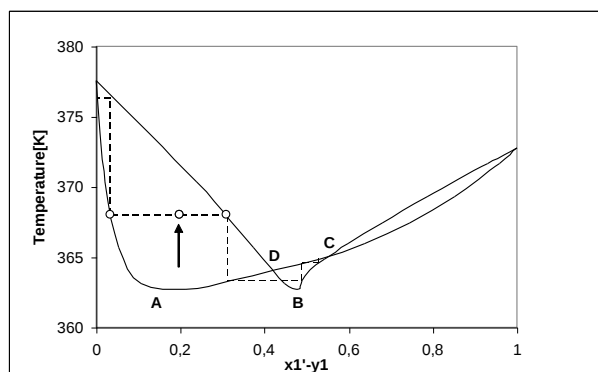


Fig. 1. Calculated T-x'-y phase diagram of 1-propanol(1)-water(2)-LiNO₃(3) ($x_3=0.06$) (experimental data obtained from Vercher *et al.* (2002)) and evolution of a hypothetical total reflux distillation.

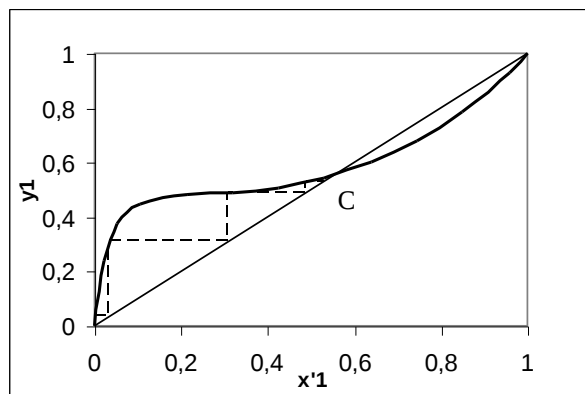


Fig. 2. Calculated isobaric x'-y diagram of 1-propanol(1)-water(2)-LiNO₃(3) ($x_3=0.06$) (experimental data obtained from Vercher *et al.* (2002)) and evolution of a hypothetical total reflux distillation.

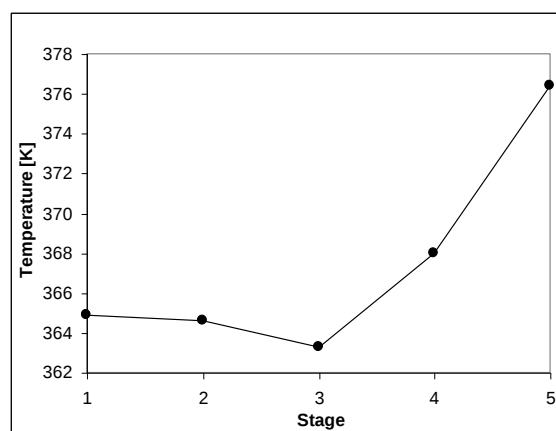


Fig. 3. Temperature profile of a hypothetical total reflux distillation (1-propanol-water-LiNO₃).

centrates and by the condensation of mixed-solvent vapor the solute dilutes, i.e. the composition of the liquid do not remain constant when phase reaction occur and an indifferent state condition is therefore not possible. It can be shown (Muzzio, 2006) that the consequence of these facts is the splitting of the binary azeotrope into the two states just mentioned above, each of which retain one of its properties⁽¹⁾.

The separation of these points depends on the concentration of the non-volatile solute, a separation which, in general, increases with increasing solute addition. In fact they may exist independently from each other. So, in Fig. 5 of the paper by Llano-Restrepo and Aguilar-Arias (2003) for the system ethanol(1) - water (2) - CaCl₂ (3) (salt concentration of 16.7 wt.% on a salt-free basis) the pseudo-azeotropic point (point C type) has already disappeared, but the state of temperature minimum (point A-B type) still remains.

The aim of this work is to simulate a distillation column with a program called GKTMM based on the Naphthali-Sandholm (1971) algorithm and the E-NRTL model, and to obtain thermodynamically consistent re-

⁽¹⁾ In terms of activity coefficients, in the case of simple regular mixtures the existence and properties of these special points have been discussed already elsewhere (Timmermann, 1987)

sults in order to get conclusions about the behavior of the temperature profile of a SED column and to help optimize the SED process in the future. Several commercial programs have also been tested, and GKTm proved to perform better than these commercial programs in the SED columns simulated. Due to its extension, this work does not include the analysis of saturated or nearly saturated systems.

II. MATHEMATICAL MODEL AND SIMULATOR

A. Software development

The simulator (GKTm v.1.2) was designed on Visual Basic (Muzzio, 2006) to solve the material, equilibrium, and energy balance (known as MEH) equations indicated by Napthali-Sandholm (1971). These equations are:

a) Material balance for component i at stage j :

$$M_{i,j} = l_{i,j} \cdot (1+s_j) + v_{i,j} \cdot (1+S_j) - l_{i,j-1} - v_{i,j+1} - f_{i,j} = 0 \quad (1)$$

b) VLE relationship for component i at stage j :

$$E_{i,j} = K_{i,j} \cdot l_{i,j} \cdot \frac{\sum_{k=1}^c v_{k,j}}{\sum_{k=1}^c l_{k,j}} - v_{i,j} = 0 \quad (2)$$

c) Energy balance at stage j :

$$H_j = H_{L_j} \cdot \sum_{i=1}^c l_{i,j} + H_{V_j} \cdot \sum_{i=1}^c v_{i,j} - H_{L_{j-1}} \cdot \sum_{i=1}^c l_{i,j-1} - H_{V_{j+1}} \cdot \sum_{i=1}^c v_{i,j+1} - H_{F_j} \cdot \sum_{i=1}^c f_{i,j} + Q_j = 0 \quad (3)$$

For this work, the following two matrices are defined:

$$\bar{X} = [\bar{X}_1, \bar{X}_2, \dots, \bar{X}_j, \dots, \bar{X}_n]^T \quad \text{and}$$

$\bar{F} = [\bar{F}_1, \bar{F}_2, \dots, \bar{F}_j, \dots, \bar{F}_n]^T$, where $\bar{X}_j$ is a vector of output variables for stage j , ordered like $\bar{X}_j = [v_{1,j}, v_{2,j}, T_j, l_{1,j}, l_{2,j}, l_{3,j}]^T$, and

$$\bar{F}_j = [H_j, M_{1,j}, M_{2,j}, M_{3,j}, E_{1,j}, E_{2,j}]^T.$$

In the Newton-Raphson method, every approximation of the result vector is calculated in the following form

$$\bar{X}^{(k+1)} = \bar{X}^{(k)} + t \cdot \Delta \bar{X}^{(k)} \quad (4)$$

where $\Delta \bar{X}^{(k)}$ can be obtained from

$$\Delta \bar{X}^{(k)} = - \left[\left(\frac{\partial \bar{F}}{\partial \bar{X}} \right)^{-1} \right]^{(k)} \cdot \bar{F}^{(k)} \quad (5)$$

and t is an arbitrary factor. In this work, t will be equal to 0.1 because it has been found that this value improves the stability of the algorithm without a significant decrease in the velocity of convergence. $\frac{\partial \bar{F}}{\partial \bar{X}}$ is the Jacobian matrix, composed by the partial derivatives of the discrepancy functions with respect to every variable. Derivatives of MEH equations, which are solved numerically, were defined by the expression

$$\frac{\partial f}{\partial x_i} \approx \frac{f(x_1, \dots, x_i + \varepsilon, \dots, x_N) - f(x_1, \dots, x_i, \dots, x_N)}{\varepsilon} \quad (6)$$

where $\varepsilon = 1.10^{-3}$. Due to the fact that analytical partial derivatives of every discrepancy functions with respect to every variable can be readily generalized to complete the Jacobian matrix $\frac{\partial \bar{F}}{\partial \bar{X}}$, the approach by finite derivatives defined in Eq. (6) was only utilized when the calculation requires the partial derivative of the VLE relationship, for instance to compute $\partial K_{i,j} / \partial T_j$. In addition, the Gauss-Jordan method of elimination with partial pivoting was used in the development of the program.

The column consists of $N+2$ stages with a condenser at stage 1, a reboiler at stage $N+2$ and without lateral streams. The pressure in the column is assumed to be constant.

As usual, the left hand side of the MEH equations is employed to define a discrepancy function and, when the value of this function is sufficiently close to zero, the program achieves the convergence. All the MEH equations are normalized to be of similar order of magnitude, in order to avoid that an error in the energy balance equation (Eq. (3)) or in the material balance (Eq. (1)) hides a more important error, for instance, in the VLE relationship (Eq. (2)). The discrepancy function is defined as follows:

$$\Psi = \left\| \bar{F} \right\| = \left(\sum_{j=1}^N \hat{H}_j^2 + \hat{M}_{1,j}^2 + \hat{M}_{2,j}^2 + \hat{M}_{3,j}^2 + \hat{E}_{1,j}^2 + \hat{E}_{2,j}^2 \right)^{1/2} \quad (7)$$

The user is able to define the limit of the convergence function; a value of 0.005 for the discrepancy function is used in this work, which avoids differences higher than 0.01K in the temperature of the stages.

In order to improve the stability of the Newton-Raphson algorithm, GKTm increases both the condenser and reboiler duties gradually. When the tolerance of the discrepancy function is reached after some internal loop iterations, the program duplicates the heat extracted from the condenser and the heat introduced through the reboiler (external loop). The solution obtained for the external loop is the seed for the next step. This process is repeated until the values of the condenser and reboiler duties are the same as the required by the user.

B. E-NRTL model

Renon and Prausnitz (1968) presented their NRTL model and, eighteen years later, Chen and Evans (1986) modified this model to adapt it to mixed-solvent electrolyte systems. From that moment on, the E-NRTL model evolved continuously.

Due to the wide acceptance in the industry and the simple calculations involved, this model has been chosen to perform correlation of phase diagrams for the systems under study in the present work.

The results obtained from the E-NRTL reported in different papers by Vercher *et al.* (1999, 2002, 2004) show the great accuracy of the model after a proper parameter regression, but the process of this regression has to be explained to expose a 'weak point' in the model.

In order to obtain the parameters of the E-NRTL model from binary data, the Solver tool of the Microsoft

Excel spreadsheet is used to minimize the objective function

$$F = \frac{1}{n} \sum_n |\gamma_{i,\text{exp}} - \gamma_{i,\text{calc}}| \quad (8)$$

Experimental data were taken from Vercher *et al.* (2002). For the binary system 1-propanol-LiNO₃ the regression-data reported by the authors are $\alpha_{13}=1.566$, $\Delta g_{13}=3.04$ kJ/mol, $\Delta g_{31}=6.64$ kJ/mol; this set of parameters gives $\Delta T=0.07$ where

$$\Delta T = (1/n) \cdot \sum_n |T_{\text{exp}} - T_{\text{calc}}| \quad (9)$$

Nevertheless, a better result ($\Delta T=0.06$) is obtained with the following parameters: $\alpha_{13}=1.566$, $\Delta g_{13}=2.02$ kJ/mol $\Delta g_{31}=6.64$ kJ/mol, where only the Δg_{13} -parameter has been changed. Finally, a still better result ($\Delta T=0.05$) is achieved using Solver with no presetting of parameters, with the following results: $\alpha_{13}=1.52$, $\Delta g_{13}=7$ kJ/mol, $\Delta g_{31}=0.50$ kJ/mol.

However, quite surprisingly, better results are obtained in the description of the ternary system using the first parameters than the third ones.

Something similar happens when parameters of the system H₂O-LiNO₃ were compared: $\alpha_{23}=0.419$; $\Delta g_{23}=15.9$ kJ/mol; $\Delta g_{32}=-7.71$ kJ/mol produces the best result ($\Delta T=0.043$) in the binary system data regression, but $\alpha_{23}=0.165$; $\Delta g_{23}=2.35$ kJ/mol; $\Delta g_{32}=-5.91$ kJ/mol ($\Delta T=0.196$) are more suitable parameters for fitting the ternary system. This unsolved problem was mentioned by Chen and Mathias (2002), stating that “these models do not always yield reliable results when extrapolated from binary systems to ternary or multicomponent systems”

The regressed parameters for both binary systems are summarized in Table 1.

In Table 2, Δf was calculated using the expression:

$$\Delta f = \frac{(|\gamma_{1-\text{exp}} - \gamma_{1-\text{calc}}| + |\gamma_{2-\text{exp}} - \gamma_{2-\text{calc}}|)}{2 \cdot N_p} \quad (10)$$

where N_p is the number of points considered. Note that in the ternary system data regression, the binary points are included.

Despite the fact that E-NRTL parameters must be regressed from ternary data because the use of binary parameters do not always yields better results when are combined to represent ternary systems, the E-NRTL model was used to describe the ternary phase diagram behavior in the program because of its simplicity and its accuracy after a proper data regression of ternary data.

III. SIMULATION RESULTS

In order to prove the functioning of GKTM, a non-salt feed system (1-propanol-water) was analyzed (input data and parameters are: Main feed flow rate ("F"): 100 kmol/h; main feed 1-propanol mole fraction ("F_{x1}"): 0.3; main feed water mole fraction ("F_{x2}"): 0.7; main feed temperature ("TF"): 362 K; main feed stage: 7; salt feed flow rate ("F"): 0 kmol/h; operating pressure("P"): 1 atm; number of equilibrium stages ("N"): 11; condenser duty ("Qc"): 0 kJ/h; reboiler duty ("Qr"): 0 kJ/h). The second set of E-NRTL parameters of Table 2 is used in the simulation as it is the one that generates the lower Δf , and the result of the simulation is shown in Fig. 4. As it can be seen, the result obtained with GKTM is thermodynamically consistent.

The main feed of the column split up into a vapor and a liquid phase with different compositions and the temperature remained constant all over the column. Fig. 4 shows that composition and temperature of both phases fit in the diagram of phases. The point A represents the input condition of the main feed which splits up in two phases represented by points L and V.

Table 1. Estimated parameters for the E-NRTL model (1-propanol-LiNO₃ and water-LiNO₃ systems)

i component	j component	α_{ij}	Δg_{ij} (kJ.mol ⁻¹)	Δg_{ji} (kJ.mol ⁻¹)	ΔT (K)
1-propanol	LiNO ₃	1.566	3.04	6.64	0.07
		1.566	2.02	6.64	0.06
		1.520	7.00	0.50	0.05
water	LiNO ₃	0.419	15.9	-7.71	0.043
		0.165	2.35	-5.91	0.196

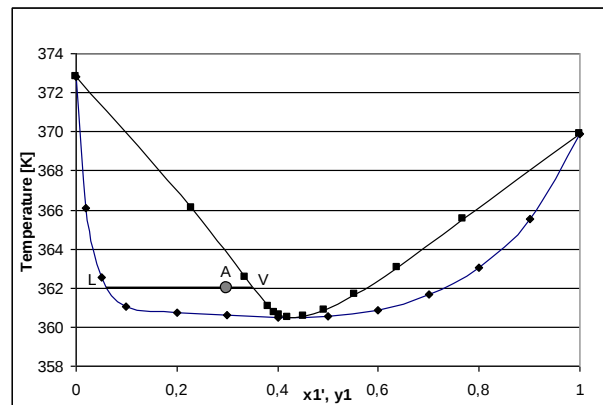


Fig. 4. T-x'-y phase diagram for the 1-propanol-water system. Point A represents the input condition.

Table 2. Estimated parameters for the E-NRTL model (1-propanol-water-LiNO₃ systems)

Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}	$\alpha_{12}=\alpha_{21}$	$\alpha_{13}=\alpha_{31}$	$\alpha_{23}=\alpha_{32}$	Δf
1648.8	7896.7	3040.0	6640.0	15900.0	-7710.0	0.477	1.566	0.419	0.232
1648.8	7896.7	3040.0	6640.0	2350.0	-5910.0	0.477	1.566	0.165	0.155
1648.8	7896.7	2020.0	6640.0	15900.0	-7710.0	0.477	1.566	0.419	0.342
1648.8	7896.7	2020.0	6640.0	2350.0	-5910.0	0.477	1.566	0.165	0.175
1648.8	7896.7	7000.0	500.0	15900.0	-7710.0	0.477	1.520	0.419	0.213
1648.8	7896.7	7000.0	500.0	2350.0	-5910.0	0.477	1.520	0.165	0.255

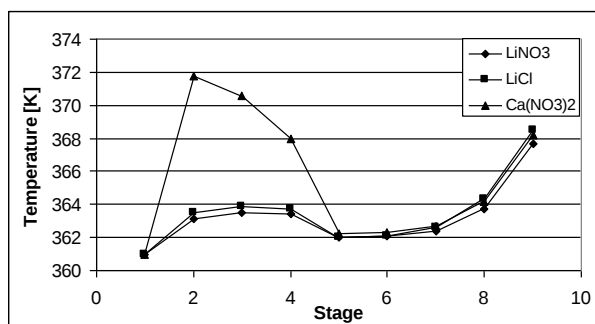


Fig. 5. Temperature versus stage. Note the local minimum at stage 5 for three mixed-solvent salt systems (1-propanol-water-LiNO₃, 1-propanol-water-LiCl and 1-propanol-water-Ca(NO₃)₂).

Table 3. Simulation results for 1-propanol-water-LiNO₃

Stage	T(K)	L(kmol/h)	V(kmol/h)	y ₁	x ₁	x ₃
1	361.0	2.4	81.3	0.377	0.072	0.000
2	363.1	3.5	83.7	0.368	0.046	0.028
3	363.5	3.5	83.9	0.357	0.041	0.028
4	363.4	3.7	83.9	0.357	0.042	0.027
5	362.0	22.1	84.0	0.356	0.050	0.005
6	362.1	22.1	2.5	0.354	0.049	0.005
7	362.4	22.1	2.5	0.346	0.045	0.005
8	363.7	22.2	2.5	0.307	0.032	0.005
9	367.7	19.7	2.5	0.185	0.012	0.005

The next step is to simulate a mixed-solvent system with a salt (1-propanol-water-LiNO₃). Input data and parameters were set as following: Main feed flow rate ("F"): 100 kmol/h; main feed 1-propanol mole fraction ("F_{x1}"): 0.3; main feed water mole fraction ("F_{x2}"): 0.7; main feed temperature ("T_F"): 362 K; main feed stage: 5; salt feed flow rate ("F"): 1 kmol/h; operating pressure ("P"): 1 atm; salt feed 1-propanol mole fraction ("Q_{x1}"): 0.9; salt feed LiNO₃ mole fraction ("Q_{x3}")=0.1; salt feed temperature ("Q_F"): 360K; salt feed stage: 2; number of equilibrium stages ("N"): 9; condenser duty ("Q_c"): -100000 kJ/h; reboiler duty ("Q_r"): 100000 kJ/h. The profile of the curve of temperature versus stage obtained from the simulation is given in Fig. 5, and a local minimum appeared in the middle of the column, as expected.

The appearance of a local minimum at stage 5 in Fig. 5 is in agreement to the diagrams of phases of the system (the one corresponding to x₃=0.06 is shown in Fig. 1). It can be readily seen that all the points reported in Table 3 belong to those diagrams.

Two additional systems (1-propanol-water-LiCl and 1-propanol-water-Ca(NO₃)₂) have been simulated under the same conditions, and added to the Fig. 5, where similar features for the three systems can be observed.

IV. CONCLUSIONS

In this work, E-NRTL is used, after a proper data regression of its parameters from ternary data, to describe a mixed solvent/salt system. This model allowed us to simulate a saline extractive distillation column, where a

notable characteristic was proven: temperature has a local extreme (minimum in the case considered) in the middle region of the column, due to the thermodynamic features of the phase diagram.

On the other hand, a technique of increase-by-step has being used to improve the stability and capability of convergence of Naphthali-Sandholm's method. This technique was included in the GKTm software, which yields to thermodynamic consistent results where other programs failed to converge.

In the literature there are many works about multiple steady states in simulation of distillation columns (e.g. the work by Bekiaris *et al.*, 2000). Although this work actually does not study the possible numerical multiplicities in the simulation of the column proposed, the solution obtained is thermodynamically consistent and the results can be taken as physically reliable.

Even though most of the authors have concentrated their attention in compositions of output and displacement of azeotropes, it is necessary to examine more deeply the whole behavior of a saline extractive distillation column in order to make accurate simulations and enhance the profitability of the entire process.

REFERENCES

- Bekiaris, N., T.E. Gütinger and M. Morari, "Multiple Steady States in Distillation: Effect of VL(L)E Inaccuracies," *AIChE J.*, **46**, 5, 955-979 (2000).
- Cardoso, M. and J. O'Connell, "Activity Coefficients in Mixed Solvents Electrolyte Solutions," *Fluid Phase Equilib.*, **33**, 315-326 (1987).
- Chen, C.C., H.L. Britt, J.F. Boston and L.B. Evans, "Local composition model for excess Gibbs energy of electrolyte systems," *AIChE J.*, **28**, 588-596 (1982).
- Chen, C.C. and L.B. Evans, "A local composition model for the excess Gibbs energy of aqueous electrolyte systems," *AIChE J.*, **32**, 444-454 (1986).
- Chen, C.C., P.M. Mathias and H. Orbey, "Use of hydration and dissociation chemistries with the electrolyte-NRTL model," *AIChE J.*, **45**, 1576-1586 (1999).
- Chen, C.C., C.P. Bokis and P. Mathias, "Segment-based excess Gibbs energy model for aqueous organic electrolytes," *AIChE J.*, **47**, 2593-2602 (2001).
- Chen, C.C. and P.M. Mathias, "Applied thermodynamics for process modeling," *AIChE J.*, **48**, 2, 194-200 (2002).
- Chen, C.C. and Y. Song, "Generalized electrolyte-NRTL model for mixed-solvent electrolyte systems," *AIChE J.*, **50**, 1928-1941 (2004).
- Cook, R.A. and W.F. Furter, "Extractive Distillation Employing a Dissolved Salt as Separating Agent," *Can. J. Chem. Eng.*, **46**, 119-123 (1968).
- Furter, W.F. and R.A. Cook, "Salt effect in distillation: a literature review," *Int. Journal of Heat and Mass Transfer*, **10**, 23-36 (1967).
- Furter, W.F. "Salt effect in distillation: a literature review II," *Can. J. Chem. Eng.*, **55**, 229-239 (1977).

- Johnson, A.I. and W.F. Furter, "Salt effect in vapor-liquid equilibrium. Part II," *Can. J. Chem. Eng.*, **38**, 78-87 (1960).
- Kablukov, I.A., *Zh. Russk. Fiz. – Khim. Obshch.* **23**, 388 (1891) (from Furter and Cook, 1967).
- Llano-Restrepo, M and J. Aguilar-Arias, "Modeling and simulation of saline extractive distillation columns for the production of absolute ethanol," *Comput. Chem. Eng.*, **27**, 527-549 (2003). erratum *Comput. Chem. Eng.*, **28**, 2851 (2004)
- Loeche, J.R. and M.D. Donohue, "Recent Advances in Modeling Thermodynamic Properties of Aqueous Strong Electrolyte Systems," *AIChE J.*, **43**, 180-195 (1997).
- Meranda, D. and W.F. Furter, "Vapor-Liquid Equilibrium in Alcohol-Water Systems Containing Dissolved Acetate Salts," *AIChE J.*, **17**, 38-42 (1971).
- Miller, W.L., *J. Phys. Chem.*, **1**, 633 (1897) (from Johnson and Further, 1960)
- Mock, B., L.B. Evans and C.C. Chen, "Thermodynamic Representation of Phase Equilibria of Mixed-Solvent Electrolyte Systems," *AIChE J.*, **32**, 1655-1664 (1986).
- Muzzio, C.R. *Sobre el efecto de un soluto no volátil en una mezcla de solventes y su aplicación en destilación extractiva*, Tesis de grado en Ingeniería Química, Facultad de Ingeniería, Universidad de Buenos Aires (2006).
- Naphtali, L.M. and D.P. Sandholm, "Multicomponent Separation Calculations by Linearization," *AIChE J.*, **17**, 48-53 (1971).
- Pinto, R.T.P, M.R. Wolf-Maciel and L. Lintomen, "Saline extractive distillation process for ethanol purification," *Comput. Chem. Eng.*, **24**, 1689-1694 (2000).
- Prigogine, I. and R. Defay, *Chemical thermodynamics*, Longmans, Green and Co. Ltd. (1954).
- Renon, H. and J.M. Prausnitz, "Local compositions in thermodynamic excess functions for liquid mixtures," *AIChE J.*, **14**, 135-144 (1968).
- Robinson, R.A. and R.H. Stokes, *Electrolyte Solutions*, 2a. Ed., Butterworths (1959).
- Sander, B., A. Fredenslund and P. Rasmussen, "Calculation of Vapour-Liquid equilibria in mixed solvent/salt systems using an Extended Uniquac Equation," *Chemical Engineering Science*. **41**, 1171-1183 (1986a).
- Sander, B., P. Rasmussen and A. Fredenslund, "Calculation of Vapour-Liquid equilibria in Nitric Acid-Water-Nitrate Salt Systems using an Extended Uniquac Equation," *Chem. Eng. Sci.*, **41**, 1185-1195 (1986b).
- Timmermann, E.O. "The effect of a non-volatile solute upon the VLE of a binary mixture of solvents. The case of simple ('regular') mixtures," *Proceedings 1st Latinamerican Symposium of "Fluid Properties and Phase Equilibria for the Chemical Process Design*, Concepción, Chile, **23**, 1-15 (1987).
- Vercher, E., F.J. Rojo and A. Martínez-Andreu, "Isobaric Vapor-Liquid Equilibria for 1-Propanol + Water + Calcium Nitrate," *J. Chem. Eng. Data*, **44**, 1216-1221 (1999).
- Vercher, E., M.I. Vázquez and A. Martínez-Andreu, "Isobaric Vapor-Liquid Equilibria for 1-Propanol + Water + Lithium Nitrate," *Fluid Phase Equilib.*, **202**, 121-132 (2002).
- Vercher, E., M.I. Vázquez and A. Martínez-Andreu, "Isobaric Vapor-Liquid Equilibria for Water + Acetic Acid + Sodium Acetate," *J. Chem. Eng. Data*, **48**, 217-220 (2003).
- Vercher, E., A. Vicent Orchillés, M. I. Vázquez, and A. Martínez-Andreu, "Isobaric Vapor-Liquid Equilibria for 1-Propanol + Water + Lithium Chloride at 100 kPa," *Fluid Phase Equilib.*, **216**, 47-52 (2004).
- Vercher, E., A.V. Orchillés, V. González-Alfaro and A. Martínez-Andreu, "Isobaric vapor-liquid equilibria for 1-propanol + water + copper(II) chloride at 100 kPa," *Fluid Phase Equilib.*, **227**, 239-244 (2005).

Received: August 27, 2012

Accepted: December 16, 2012

Recommended by Subject Editor: Mariano Martín