Simulation of a Distillation Column on an IBM PC, Accounting for Real Behaviour of Electrolyte Solutions*

André Bosen and Manfred Roth**

This contribution demonstrates the possibility of using a thermodynamic description of electrolyte solutions directly for computer simulation of distillation columns. Coefficients are determined for a combination of a solvation model with a local composition equation for the activity coefficient. The use of one set of coefficients yields good results of calculation of vapour pressure, vapour phase composition and caloric data of hydrochloric acid. Solution of material and heat balance equations of distillation columns is achieved on an IBM PC with the above description. Two illustrative examples of an absorption and a rectification calculation are presented.

1 Introduction

Process design of chemical plants by computer simulation requires the knowledge of physical properties of fluids for the design of industrial equipment. Distillation columns are very important in many chemical plants. The present contribution deals with complex columns for multicomponent distillation. The simulation of distillation columns is not a new topic but, nevertheless, it leads to severe problems if electrolyte solutions are present. The description of phase equilibria of electrolyte solutions, such as hydrochloric or sulphuric acid, is difficult because of strong non-ideality of these azeotropic systems.

A program based on a thermodynamic description [2] performed on an IBM-PC for the system H₂O-HCl is used for successful simulations of distillation and absorption columns.

2 Description of Electrolyte Solutions

The thermodynamic description combines an equation for the activity coefficients (NRTL [5], Wilson [6]) with a solvation model [2], which accounts for the internal grouping within the liquid phase.

The vapour pressure of any component is calculated from

\[ p_i = x_i \gamma_i p_i^0 \]  

(1)

where \( p_i \) is the partial pressure, \( x_i \) the mole fraction of the liquid phase, \( \gamma_i \) the activity coefficient and \( p_i^0 \) the vapour pressure of pure substance.

This includes the assumptions that the vapour behaves as an ideal gas and the liquid is incompressible. These simplifications are permissible in view of the investigated pressure range. The application of a local composition model such as the Wilson and NRTL equations for the activity coefficient gives satisfactory results only for non-electrolyte solutions.

With the introduction of a solvation model, we perform an equilibrium reaction, which alters the composition in the liquid. Both Wilson and NRTL equations use these new compositions. This model takes into account the dissociation of the electrolyte and the formation of a solvent cloud. This will be referred to as cluster C⁺, C⁻ and is shown in Fig. 1.

Let the number of dissociation products be \( \nu \) (for hydrochloric acid \( \nu = 2 : H^+ \) and \( Cl^- \)). The total number of solvent molecules which are bound in \( \nu \) clusters is denoted by \( m \) (in Fig. 1: \( m = 3 \)). Owing to absence of ions in the vapour, vapour pressure of the clusters is neglected. For computer programs, this solvation model can be regarded as a UNIT. INPUT are the mole fractions when solvation is not considered while OUTPUT are those mole fractions when solvation is considered (Fig. 2); then \( p_i = x_i \gamma_i p_i^0 \).

The solvation reaction is described with an equilibrium constant \( K_a \), which gives the missing equation for the cluster mole fraction. In total, we obtain a set of non-linear Eqs (2), (3) and (4).

\[ m \quad \overset{\text{H}_2\text{O}}{\text{+}} \quad \overset{\text{HCl}}{\text{\rightarrow}} \quad \overset{\text{Cl}^-}{\text{+}} \quad \overset{\text{H}^+}{\text{+}} \quad \overset{\text{H}_2\text{O}}{\text{\rightarrow}} \quad \overset{\text{C}^\pm}{\text{C}} \]

Fig. 1. Solvation model.

\[ x_0 \quad \overset{\text{SOLVATION UNIT}}{\text{\rightarrow}} \quad x_1 \quad \overset{x_2}{x_3} \quad x_c \]

Fig. 2. Solvation UNIT.

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1) List of symbols at the end of the paper.

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\[ x_S = x_S^0 + x_C \left[ x_S^0 (m + 1 - \nu) - m \right], \quad (2) \]
\[ x_E = x_E^0 + x_C \left[ x_E^0 (m + 1 - \nu) - 1 \right], \quad (3) \]
\[ K_a = \frac{x_C}{x_S x_E} \frac{y_C}{y_S y_E}. \quad (4) \]

(Note: \( 1 = x_S + x_E + \nu x_C \))

2.1 Enthalpy of Solution

In order to formulate an energy balance, one needs the caloric data. Molar enthalpy of the solution must be calculated with the following equation:

\[ h = \frac{1}{1 + x_C (m + 1 - \nu)} \left( h_C^0 + x_C RT^2 \frac{\partial \ln K_a}{\partial T} \right) + x_S^0 h_S^0 + x_E^0 h_E^0. \quad (5) \]

2.2 Approximation

To use the above equations, the values of \( \gamma_i \), \( K_a \) and \( m \) must be known. They result from an approximation to experimental data, where coefficients (the relationship will be stated later) are adapted.

Experimental data on total pressure, vapour phase composition and caloric values were obtained to determine the coefficients by the following method.

\[ \sum_i I \left( \frac{y_i^\text{EXP} - y_i^\text{CAL}}{y_i^\text{EXP}} \right)^2 = \text{minimum}. \]

EXP: experimental data point,
CAL: calculated value,
\( I \): number of data points.

One set of coefficients is obtained which yields satisfactory results for all the experimental data. Several systems are described, using the solvation model e.g. [1, 3].

The quality of this description will be illustrated by a comparison of calculated and experimental data for hydrochloric acid (Fig. 3 and Table 1). The diagrams are based on the Wilson equation.

2.3 Equations and Coefficients

2.3.1 Wilson Equation [6]

Activity coefficient:

\[ \ln \gamma_i = 1 - \ln \left( \sum_j x_j A_{ij} \right) - \sum_k \frac{x_k A_{ki}}{\sum_j x_j A_{kj}}. \quad (6) \]

![Figure 3. Comparison of calculated (−) and experimental (+, o) values. System: H₂O-HCl.](image)

Table 1. Experimental data of the system hydrochloric acid.

<table>
<thead>
<tr>
<th></th>
<th>Number of data points</th>
<th>Relative deviation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wilson mean</td>
<td>max.</td>
</tr>
<tr>
<td>All values</td>
<td>534</td>
<td>2.3</td>
</tr>
<tr>
<td>Total pressure</td>
<td>275</td>
<td>2.2</td>
</tr>
<tr>
<td>Vapour phase composition</td>
<td>119</td>
<td>2.2</td>
</tr>
<tr>
<td>Heat of dilution</td>
<td>140</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Molar excess enthalpy:

$$h^E = RT^2 \sum_j x_j \frac{\sum_i \frac{\partial A_{ij}}{\partial T}}{\sum_j x_j A_{ij}} ,$$

$$A_{ij} = \exp(a_{ij} + b_{ij} T) ,$$

$$\frac{\partial A_{ij}}{\partial T} = A_{ij} b_{ij} ,$$

$$A_{ii} = A_{jj} = 1 .$$

System: Hydrochloric acid, $K_a = \exp(-7.1 + 4474/T)$.

$$\frac{\partial \ln K_a}{\partial T} = -\frac{4474}{T^2} ,$$

$$\nu = 2 ; m = 4 ; N = 4 \text{ (considering solvation)}. $$

The results are shown in Table 2.

### 2.3.2 NRTL Equation [5]

Activity coefficient:

$$\ln \gamma_i = \frac{\sum_j \tau_{ij} G_{ij} x_j}{\sum_j x_j G_{ij}} + \sum_k \frac{x_k G_{jk}}{\sum_j x_j G_{jk}} \left( \tau_{ik} - \frac{\sum_n \tau_{nk} G_{nk} x_n}{\sum_j x_j G_{jk} x_j} \right) ,$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) .$$

Molar excess enthalpy:

$$h^E = -RT^2 \sum_i x_i \frac{u'v - v'u}{v^2} ,$$

$$u = \sum_j \tau_{ij} G_{ij} x_j$$

$$u' = \sum_j \left( x_j \frac{\partial \tau_{ij}}{\partial T} G_{ij} + \tau_{ij} \frac{\partial G_{ij}}{\partial T} \right) ,$$

$$v = \sum_k G_{ki} x_k$$

$$v' = \sum_k x_k \frac{\partial G_{ki}}{\partial T} ,$$

$$\tau_{ij} = a_{ij} + b_{ij} / T ,$$

### Table 2. Wilson equation: Coefficients of the system H$_2$O (i = 1)-HCl (i = 2)–cluster (i = 3,4) [3]:

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>$a_{ij}$</th>
<th>$b_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>5.351</td>
<td>-0.0091</td>
</tr>
<tr>
<td>1</td>
<td>3,4</td>
<td>0.371</td>
<td>-0.0014</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1.342</td>
<td>0.0048</td>
</tr>
<tr>
<td>2</td>
<td>3,4</td>
<td>8.505</td>
<td>-0.0289</td>
</tr>
<tr>
<td>3,4</td>
<td>1</td>
<td>5.269</td>
<td>-0.0161</td>
</tr>
<tr>
<td>3,4</td>
<td>2</td>
<td>7.790</td>
<td>-0.0160</td>
</tr>
</tbody>
</table>

For the simulation, a hypothetical system is considered, represented by the model column in Fig. 4. The first stage corresponds to a condenser (partial, total or compound), the last stage to a reboiler. Each stage is assumed to be an equilibrium stage (Fig. 5).

### Table 3. NRTL equation: Coefficients of the system H$_2$O (i = 1)-HCl (i = 2)-cluster (i = 3,4).

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>$a_{ij}$</th>
<th>$b_{ij}$</th>
<th>$\alpha_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3.164</td>
<td>1710.0</td>
<td>-0.257</td>
</tr>
<tr>
<td>1</td>
<td>3,4</td>
<td>-1.802</td>
<td>-221.1</td>
<td>-0.149</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-0.527</td>
<td>-998.1</td>
<td>-0.257</td>
</tr>
<tr>
<td>2</td>
<td>3,4</td>
<td>2.455</td>
<td>-329.4</td>
<td>-0.336</td>
</tr>
<tr>
<td>3,4</td>
<td>1</td>
<td>3.722</td>
<td>-1128.0</td>
<td>-0.149</td>
</tr>
<tr>
<td>3,4</td>
<td>2</td>
<td>-0.110</td>
<td>-862.1</td>
<td>-0.336</td>
</tr>
</tbody>
</table>

Fig. 4. Distillation column.
The set of equations, which must be solved for a component \(i\), is formulated as follows:

**Material balance equation around stage \(j\)**

\[ 0 = L_{j-1}x_{i,j-1} - (V_j + S_{V,j})y_{i,j} - (L_j + S_{L,j})x_{i,j} - F_j x_{F,i,j} \]  

**Heat balance equation around stage \(j\)**

\[ 0 = L_j h_{L,j-1} + V_{j+1} h_{V,j+1} - (V_j + S_{V,j}) h_{V,j} - (L_j + S_{L,j}) h_{L,j} + F_j h_{F,j} + Q_j \]  

The liquid flow rates are expressed as functions of \(V\)'s by an overall material balance of all stages from condenser (stage 2) through \(j^{th}\) stage

\[ L_j = V_{j+1} + \sum_{k=2}^{j} (F_k - S_{V,k} - S_{L,k}) - D \]  

In this paper, we assume the knowledge of feed \((F, x_F)\), the product purities \((y_1, x_1)\) at the condenser and the reboiler (product streams \(V_1, L_1\) from total material balance) and the reflux RF

\[ RF = \frac{D}{L_1} \]  

One may obtain a constant pressure or a pressure drop across the stage. Independent variables are the mole fractions of liquid \(x_{ij}\) \((1 \leq i \leq N - 1, 1 \leq j \leq n)\) and the vapour rate profile \(V_1\) to \(V_n\); therefore one obtains the heats of reboiler and condenser \(Q_n\) and \(Q_1\). For a conventional column, all other quantities of the external streams are zero.

The mole fractions of vapour phase \(y_{ij}\), temperature \(T_j\) and enthalpy \(h_j\) are obtained from the thermodynamic description:

\[ T = f(x, p), \]
\[ y = f(x, T, p), \]
\[ h = f(x, y, T) \]  

Eqs (14) and (15) are solved sequentially. The first step is to formulate an initial set of \(x_{ij}\) and \(V_j\). Then, the non-linear equations of the material balance (14) are solved by a program from the IMSL library [4]. Values of \(x_{ij}\) are determined and used in Eq. (15); this yields new values of \(V_j\). If the new set of values deviates (tolerance \(\varepsilon\)) from the initial set, Eq. (14) must be solved again.

After the last iteration step, the heats of condenser and reboiler are determined. The computational procedure is shown in a block diagram, Fig. 6.

### 3.1 Initial Set of Values

For the initial step, we assumed that the molar heats of vaporization of the components are equal and, for this reason, \(L_j\) and \(V_j\) are constant throughout the column; the material balance can be solved directly, the result being the initial mole fractions of liquid and the number of stages at a given reflux and the required purity of product streams.

The vapour rate profile \(V_j\) is then assumed to be linear from reboiler to condenser. The initial values are accurate enough, so that the PC program will converge.

### 3.2 Illustrative Examples

Two numerical examples for hydrochloric acid are as follows. For practical reasons, results are converted into mass related values. In the first example, a product of 99 wt-% HCl is obtained from a 28 wt-% feed.

In the second example, a stream of 17 wt-% HCl is concentrated to 31 % with gaseous HCl.

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**Fig. 5. Ideal equilibrium stage.**

**Fig. 6. Block diagram.**
3.2.1 Example 1 (Figs 7–9)

Stage number \( n = 13 \); Feed stage \( j = 5 \); Reflux \( RF = 1.5 \).

**FEED:** 
- \( F = 100.0 \text{kg/h, } t = 96.4^\circ\text{C, } x_F = 28.3\text{wt-%HCl} \)

**PRODUCT:**
- Reboiler: \( L_n = 90.7 \text{kg/h, } t = 107.7^\circ\text{C, } x_n = 21.1\text{wt-%} \), \( Q = 29.4 \text{MJ/h} \)
- Condenser: \( D = 9.3 \text{kg/h, } t = 47.6^\circ\text{C, } y_1 = 99\text{wt-%} \), \( Q = 17.7 \text{MJ/h} \)

3.2.2. Example 2 (Figs 10–12)

Stage number \( n = 9 \); Feed 1 stage \( j = 3 \), Feed 2 stage \( j = 9 \); Reflux \( RF = 0.5 \).

**FEED:** 
- \( F_1 = 100.0 \text{kg/h, } t = 70.0^\circ\text{C, } x_F = 16.7\text{wt-%HCl} \)
- \( F_2 = 19.5 \text{kg/h, (gaseous HCl)} \)

**PRODUCT:**
- Bottom: \( L_n = 117.4 \text{kg/h, } t = 86.6^\circ\text{C, } x_n = 30.8\text{wt-%} \), Condenser: \( D = 2.1 \text{kg/h, } t = 104.4^\circ\text{C, } y_1 = 1.7\text{wt-%} \), \( Q = 2.3 \text{MJ/h} \).
Symbols used

- \( a_{ij}, b_{ij} \): parameters in determination of activity coefficients
- \( D \): distillation rate
- \( F \): feed
- \( G_{ij} \): NRTL parameter
- \( h \): molar enthalpy
- \( h^e \): molar excess enthalpy
- \( h_i^0 \): molar enthalpy of pure substance \( i \)
- \( K_s \): equilibrium constant
- \( L_j \): liquid flow rate, stage \( j \)
- \( m \): solvation number
- \( N \): number of components
- \( n \): number of stages
- \( p_i \): partial pressure
- \( p_i^0 \): vapour pressure of pure component \( i \)
- \( Q \): heat duty
- \( R \): gas constant
- \( RF \): reflux
- \( S \): side stream
- \( T \): absolute temperature
- \( t \): temperature (°C)
- \( V_j \): vapour flow rate, stage \( j \)
- \( x_i \): mole fraction when solvation is considered
- \( x_i^0 \): mole fraction when solvation is neglected
- \( y_i \): mole fraction of vapour phase
- \( y_{\text{EXP}} \): experimental data (pressure, vapour composition, enthalpy)
- \( y_{\text{CAL}} \): calculated value

Greek symbols

- \( \alpha_{ij} \): NRTL parameter
- \( \gamma_i \): activity coefficient
- \( \Lambda_{ij} \): Wilson parameter
- \( \nu \): number of dissociation products
- \( \tau_{ij} \): NRTL parameter

Indices

- \( S \): solvent
- \( E \): electrolyte
- \( C \): cluster

References