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The Rachford-Rice equation: application to ternary diagram

A equação de Rachford-Rice: aplicação ao diagrama ternário

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Ternary phase diagrams in liquid-liquid equilibrium, for the water-ethanol-ethyl acetate system, were calculated and the results presented in rectangular and triangular diagrams. Initially, the thermodynamical background and the conditions of equilibrium are presented, involving the equality of activities and the mass balance condition. From this system of equations, the Rachford-Rice equation is deduced, transforming the problem of eight equations into a problem of one equation with one unknown. The Non-Random-Two-Liquid model was adopted to calculate activity coefficients, but other models can be easily adapted. An algorithm is presented to calculate the equilibrium compositions of this ternary system, together with numerical results. The theoretical-experimental comparison is in fair agreement, showing the robustness and simplicity of the Rachford-Rice equations. The material presented here is accessible to undergraduate students.

Keywords: Rachford-Rice, ternary system, liquid-liquid equilibrium.

O equilíbrio líquido-líquido no sistema água-etanol-acetato de etila foi calculado e os resultados foram apresentados em diagramas retangulares e triangulares. Inicialmente, o contexto termodinâmico e as condições de equilíbrio são apresentados, envolvendo a igualdade das atividades e o balanço de massas. A equação de Rachford-Rice é deduzida das oito condições de equilíbrio termodinâmico. Definindo uma nova variável, razão de atividades, esse problema de oito variáveis independentes é transformado em um problema de uma variável independente. Serão apresentadas aplicações, adotando-se o modelo de atividade Non-Random-Two-Liquid, para um equilíbrio ternário, considerando o sistema água-etanol-acetato de etila. Os resultados são apresentados em diagramas retangulares e triangulares. É feita comparação com experimental, mostrando a qualidade e simplicidade da equação de Rachford-Rice. Um algoritmo é apresentado para se calcular as composições de equilíbrio, tornando o material aqui apresentado mais acessível aos alunos de graduação.

Palavras-chave: Rachford-Rice, sistema ternário, equilíbrio líquido-líquido.

1. Introduction

The interpretation of many experimental results in ternary phase diagrams can be a challenging subject, usually discussed in a qualitative way. The theoretical point of view of ternary phase diagrams is not even addressed in physics and chemistry textbooks, with the topic being restricted to one component, under the Clausius-Clapeyron equation or to two components, most often using a short range lattice model [1, 2] or several other models, such as the free volume theory [3]. But liquids have also a long range important interaction that must be considered. Solution of the Ornstein-Zernick equations [4, 5] has to be carried out if a more precise nature of the liquid state is to be investigated. Although the Ornstein-Zernick equations can be adapted to the molecular case, with a mean potential, these are equations complex to solve [6, 7] and not adequated for an undergraduated course.

Therefore, a more suitable formulation is needed to explain the ternary equilibrium in the molecular liquid phase. Surprisingly enough, this important step in the study of the liquid-liquid equilibrium was formulated long ago, by Rachford and Rice [8] and certainly not explored in teaching termodynamics in physics and chemistry courses, although more popular in the engineering area [9]. These equations, the Rachford-Rice equations, will be discussed and applied to a ternary phase diagram in the present work . A thermodynamical background together with equilibrium conditions will be explained, from which the Rachford-Rice equations will be established. As to be shown, there is no need to use elaborate optimization techniques to solve coupled thermodynamic equations, since the problem is transformed into a one independent variable.

Numerical results for the system, water, ethanol and ethyl acetate, will be discussed under the NRTL (Non Random Two Liquid) activity model [10, 11]. These components will be labeled by the numbers 1, 2 and 3, respectively. The material presented in this article will

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*Correspondence email address: jpbraga@ufmg.br allow the reader to predict a ternary diagram, thus complementing the study on phase diagrams. The theory is not restricted to three components and can easily be adapted to more components or to other activity coefficient models.

2. Thermodynamical Background

The Gibbs energy differential form can be expressed as, $dG = -SdT + Vdp + \sum_i \mu_i dN_i$ or $dG = \sum_i d\mu_i N_i + \sum_i \mu_i dN_i$, as elaborated in basic thermodynamics courses [12], with the variables having their usual meaning. Comparing these two results, results in,

$$SdT - Vdp + \sum_i N_i d\mu_i = 0 \tag{1}$$

known as the Gibbs-Duhem equation for the Gibbs energy. For fixed temperature and pressure,

$$\sum_i N_i d\mu_i = 0 \tag{2}$$

a particular case of the Gibbs-Duhem equation, if applied to Gibbs energy. Although the proof of the Gibbs-Duhem equation was given for the Gibbs energy, the relationship is more general and expressed as [13],

$$\sum_i N_i d\overline{f}_i = 0 \tag{3}$$

with $\overline{f}_i = \left(\frac{\partial f}{\partial N_i}\right)_{T,p,N_j}$ the partial molar quantity. If f is the Gibbs energy, equation (2) is recovered. However, the quantity f can take on any homogeneous function of degree one (extensive thermodynamic quantity), such as other energies, volume or entropy [14].

Gilbert Lewis [15] introduced the concept of activity in thermodynamics as,

$$\mu(T,p) = \mu^0(T) + RT \ln a \tag{4}$$

with a representing the activity. The activity coeficient, γ, is then defined in the form

$$a = \gamma x \tag{5}$$

representing a departure from the mole fraction. For the ideal system, $\gamma = 1$, which is taken as a reference to calculate excess energies. Therefore, for the excess Gibbs energy,

$$\begin{aligned} G_i^E &= (\mu^0(T) + RT\ln x_i + RT\ln\gamma_i) \\ &\quad - (\mu^0(T) + RT\ln x_i) \\ &= RT\ln\gamma_i \end{aligned} \tag{6}$$

or for many components,

$$G^E = RT\sum_i x_i \ln\gamma_i \tag{7}$$

expression to be used along the present work.

A model for the activity coefficient has to be proposed in order to calculate other thermodynamics properties. From $d\mu_i(T,p) = RTd\ln a_i$ one can develop,

$$\begin{aligned} \frac{x_1 d\mu_1 + x_2 d\mu_2}{RT} &= x_1 d(\ln a_1) + x_2 d(\ln a_2) \\ &= x_1 d(\ln x_1) + x_2 d(\ln x_2) + x_1 d(\ln\gamma_1) \\ &\quad + x_2 d(\ln\gamma_2) \\ &= 0 \end{aligned} \tag{8}$$

or,

$$x_1 d(\ln\gamma_1) + x_2 d(\ln\gamma_2) = 0 \tag{9}$$

since $x_1 d(\ln x_1) + x_2 d(\ln x_2) = 0$. For many components,

$$\sum x_i d(\ln\gamma_i) = 0 \tag{10}$$

This form of the Gibbs-Duhem equation is useful for testing the validity of various activity coefficient models. Any proposed model must satisfy this equation.

3. Conditions of Equilibrium

For a three-component liquid-liquid equilibrium with two phases, α and β, the equality of chemical potentials leads to the equality of activities, $a_i^\alpha = a_i^\beta$, $i = 1,2,3$, where $a_i^p = \gamma_i^p x_i^p$, with p indicating the phase, γ denoting the activity coefficient, and x representing the mole fraction. Number of particles conservation in each phase establishes two more equations, $x_1^p + x_2^p + x_3^p = 1,\ p = \alpha,\beta$. Also, these particles will be either in phase α and phase β, that is, $P^\alpha + P^\beta = 1$, with P representing the relative mole fraction of each phase p.

Two mass balances can also be taken into account, $x_i^\alpha P^\alpha + x_i^\beta P^\beta = z_i$, $i = 1,2$. Therefore, there will be eight coupled equations,

$$\begin{aligned} &\gamma_1^\alpha x_1^\alpha = \gamma_1^\beta x_1^\beta \\ &\gamma_2^\alpha x_2^\alpha = \gamma_2^\beta x_2^\beta \\ &\gamma_3^\alpha x_3^\alpha = \gamma_3^\beta x_3^\beta \\ &x_1^\alpha P^\alpha + x_1^\beta P^\beta = z_1 \\ &x_2^\alpha P^\alpha + x_2^\beta P^\beta = z_2 \\ &x_1^\alpha + x_2^\alpha + x_3^\alpha = 1 \\ &x_1^\beta + x_2^\beta + x_3^\beta = 1 \\ &P^\alpha + P^\beta = 1 \end{aligned} \tag{11}$$

with eight unknows, x_1^α, x_1^β, x_2^α, x_2^β, x_3^α, x_3^β, P^α e P^β. The relation $x_3^\alpha P^\alpha + x_3^\beta P^\beta = z_3$ would be redundant and does not need to be considered in the numerical solution.

The use of $x_3^\alpha = 1 - x_1^\alpha - x_2^\alpha$, $x_3^\beta = 1 - x_1^\beta - x_2^\beta$ and $P^\beta = 1 - P^\alpha$ further reduces the system of eight equations to a system of five equations with five unknowns, implicitly satisfying the conservation of mass. With the global compositions provided and a suitable activity coefficient model, this system of non-linear equations can be solved numerically.

4. The Rachford-Rice Equation

Although the numerical solution of the system of equation (11) is possible, the problem can still be drastically simplified, being reduced to a problem with one unknown. This is the essence of the Rachford-Rice equation, to be discussed. Defining,

$$K_i = \frac{x_i^\alpha}{x_i^\beta} = \frac{\gamma_i^\beta}{\gamma_i^\alpha} \tag{12}$$

one develops,

$$\begin{aligned} z_i &= P^\alpha x_i^\alpha + P^\beta x_i^\beta = P^\alpha x_i^\alpha + (1 - P^\alpha) x_i^\beta \\ &= P^\alpha x_i^\alpha + (1 - P^\alpha)\frac{x_i^\alpha}{K_i} \end{aligned} \tag{13}$$

Multiplying by K_i and rearranging the terms,

$$\begin{aligned} K_i z_i &= P^\alpha K_i x_i^\alpha + (1 - P^\alpha) x_i^\alpha = (1 - P^\alpha + P^\alpha K_i) x_i^\alpha \\ &= [1 + P^\alpha (K_i - 1)] x_i^\alpha \end{aligned} \tag{14}$$

Therefore,

$$\begin{aligned} x_i^\alpha &= \frac{K_i z_i}{1 + P^\alpha (K_i - 1)} \\ x_i^\beta &= \frac{z_i}{1 + P^\alpha (K_i - 1)} \end{aligned} \tag{15}$$

in which $x_i^\beta = \frac{x_i^\alpha}{K_i}$ was used for the second equation.

Number of particle conservation is expressed by, $F = \sum_i x_i^\alpha - \sum_i x_i^\beta = 0$, or,

$$\sum_{i=1}^{m} \frac{z_i (K_i - 1)}{1 + P^\alpha (K_i - 1)} = 0 \tag{16}$$

The relative mole fraction P^α is the only unknown in this equation. Result (16) is general and does not depend on components number. Summation has to be carried out for all species, as stated. The equation can also be set in a more compact form, defining

$$\sum_{i=1}^{m} \frac{z_i}{c_i + P^\alpha} = 0 \tag{17}$$

with $c_i = \frac{1}{K_i - 1}$. Expressions, $x_i^\alpha = \frac{z_i (c_i + 1)}{c_i + P^\alpha}$ and $x_i^\beta = \frac{z_i c_i}{c_i + P^\alpha}$ can also be used, if the constant c_i is introduced. Equation (17) is more atractive for numerical and analytical analysis. Equation (17), a simple and elegant relation, is the Rachford-Rice equation.

5. The NRTL Activity Coefficient Model

The quantity K_i will depend on the species compositions, or activity coefficient, and must be updated for each new concentration value, if the Rachford-Rice solution is to be found. It is therefore necessary that a model of this quantity be established. Among the possible models for activity coefficients, the one that became most suitable, as it combined efficiency, simplicity and provided analytical expressions for the case of three components, was the NRTL (Non Random Two Liquid) model [16]. The NRTL model, like the Wilson, UNIQUAC, and UNIFAC models, belongs to the category of local composition models, where the composition around a molecule differs from the bulk composition [16]. Several other activity coefficient models are possible and described in the literature, such as the Margules model, the van Laar model and the Flory-Huggins [16] model. However, as will be shown, the NRTL model was sufficient for the purposes of the present work.

From measurements of the excess Gibbs energy, $G^E = G^E(T, p, N_1, N_2, \ldots, N_p)$, it is possible to establish the activity coefficients, from which the thermodynamical properties can be inferred. The relationship between the excess Gibbs energy and the activity coefficient is essential, as activity coefficients are deduced from Gibbs energy models.

Activity coefficients for a binary system in the NRTL model are given by [16],

$$\begin{aligned} \ln \gamma_1 &= x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12} \tau_{12}}{(x_2 + x_1 G_{12})^2} \right] \\ \ln \gamma_2 &= x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{G_{21} \tau_{21}}{(x_1 + x_2 G_{21})^2} \right] \end{aligned} \tag{18}$$

in which G_{12}, G_{21}, τ_{12} e τ_{21} are constants. From $\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$ one can deduce,

$$\begin{aligned} \frac{G^E}{x_1 x_2 RT} &= \tau_{21} G_{21} \frac{x_2 G_{21}}{(x_1 + x_2 G_{21})^2} + x_2 \frac{G_{12} \tau_{12}}{(x_2 + x_1 G_{12})^2} \\ &+ x_1 \tau_{12} (\frac{G_{12}}{x_2 + x_1 G_{12}})^2 + x_1 \frac{G_{21} \tau_{21}}{(x_1 + x_2 G_{21})^2} \end{aligned} \tag{19}$$

Rearranging the terms,

$$\frac{G^E}{x_1 x_2 RT} = \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} + \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} \tag{20}$$

This is the Gibbs energy for the binary case, when considering the NRTL model. The equations (18) and (20) are thermodynamically consistent, as they satisfy the Gibbs-Duhem equation [12].

Despite involving a much more laborious algebra, the excess Gibbs energy and activity coefficient relationship are established in an analogous way for the case of many components. The excess Gibbs energy, for a system of m components adopting the NRTL model, is given by [16],

$$\frac{G^E}{RT} = \sum_{i=1}^{m} x_i \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} \tag{21}$$

with,

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \cdot \left(\tau_{ij} - \sum_{i=1}^{m} x_i \frac{\sum_{r=1}^{m} \tau_{rj} G_{rj} x_r}{\sum_{l=1}^{m} G_{lj} x_l} \right) \tag{22}$$

For three components, $m = 3$,

$$\begin{aligned} \ln \gamma_i = {} & \frac{\tau_{1i} G_{1i} x_1 + \tau_{2i} G_{2i} x_2 + \tau_{3i} G_{3i} x_3}{G_{1i} x_1 + G_{2i} x_2 + G_{3i} x_3} \\ & + \frac{x_1 G_{i1}}{G_{11} x_1 + G_{21} x_2 + G_{31} x_3} \\ & \cdot \left(\tau_{i1} - \frac{x_1 \tau_{11} G_{11} + x_2 \tau_{21} G_{21} + x_3 \tau_{31} G_{31}}{G_{11} x_1 + G_{21} x_2 + G_{31} x_3} \right) \\ & + \frac{x_2 G_{i2}}{G_{12} x_1 + G_{22} x_2 + G_{32} x_3} \\ & \cdot \left(\tau_{i2} - \frac{x_1 \tau_{12} G_{12} + x_2 \tau_{22} G_{22} + x_3 \tau_{32} G_{32}}{G_{12} x_1 + G_{22} x_2 + G_{32} x_3} \right) \\ & + \frac{x_3 G_{i3}}{G_{13} x_1 + G_{23} x_2 + G_{33} x_3} \\ & \cdot \left(\tau_{i3} - \frac{x_1 \tau_{13} G_{13} + x_2 \tau_{23} G_{23} + x_3 \tau_{33} G_{33}}{G_{13} x_1 + G_{23} x_2 + G_{33} x_3} \right), \\ & \qquad i = 1, 2, 3. \end{aligned} \tag{23}$$

These relations are to be used in the Rachford-Rice equations numerical solution, with the constants calculated from experimental data and taken from the literature [10, 11]. For the data presented in Table 1, one has to use,

$$\begin{aligned} \tau_{ij} &= \frac{A_{ij}}{RT}, \quad \tau_{ii} = 0 \\ G_{ij} &= e^{-\tau_{ij} \alpha_{ij}}, \quad G_{ii} = 1 \end{aligned} \tag{24}$$

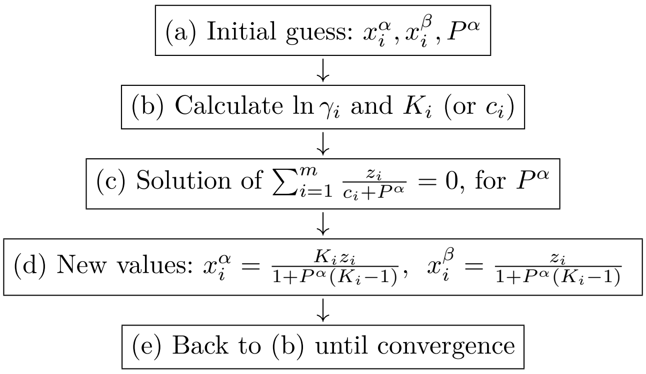
in equation (23).

Table 1: Parameters for the water-ethanol-ethyl acetate system in the NRTL model.

A_{ij}/cal mol^{-1}	α_{ij}
$A_{12} = 576.3763$	$\alpha_{12} = 0.2533$
$A_{21} = -27.8280$	$\alpha_{21} = 0.2533$
$A_{13} = 2655.3$	$\alpha_{13} = 0.3366$
$A_{31} = 805.5448$	$\alpha_{31} = 0.3366$
$A_{23} = -670.9500$	$\alpha_{23} = 0.2464$
$A_{32} = 990.8621$	$\alpha_{32} = 0.2464$

6. Solving the Rachford-Rice Equation

For a given global composition z_i ($i = 1, 2, 3$), the Rachford-Rice equation can be solved following the steps:



(a) Initial guess: $x_i^\alpha, x_i^\beta, P^\alpha$

(b) Calculate $\ln \gamma_i$ and K_i (or c_i)

(c) Solution of $\sum_{i=1}^{m} \frac{z_i}{c_i + P^\alpha} = 0$, for P^α

(d) New values: $x_i^\alpha = \frac{K_i z_i}{1 + P^\alpha (K_i - 1)}$, $x_i^\beta = \frac{z_i}{1 + P^\alpha (K_i - 1)}$

(e) Back to (b) until convergence

Step (b) is the most elaborate in solving the Rachford-Rice equation, as it involves the calculation of the activity coefficient and the constant K_i, but for each iteration this value is fixed, as the compositions are predefined. The process will be illustrated for each iteration, that is, for a fixed K_i.

Suppose that in the considered iteration, the constants are, $c_1 = -1.4403$, $c_2 = 0.5640$, $c_3 = 0.0243$ and $z_1 = 0.6310$, $z_2 = 0.0315$, $z_3 = 0.3375$. The solution of the Rachford-Rice,

$$\frac{z_1}{c_1 + P^\alpha} + \frac{z_2}{c_2 + P^\alpha} + \frac{z_3}{c_3 + P^\alpha} = 0 \tag{25}$$

has to be found and can be carried out in different ways, as a simple command in computational packages, or by using the Newton-Raphson method, resulting in the value of P^α for the considered step. However, the situation is even simpler. Rearranging equation (25),

$$\begin{aligned} (P^\alpha)^2 &+ (c_2 z_1 + c_3 z_1 + c_1 z_2 + c_3 z_2 + c_1 z_3 + c_2 z_3) P^\alpha \\ &+ (c_2 c_3 z_1 + c_1 c_3 z_2 + c_1 c_2 z_3) = 0 \end{aligned} \tag{26}$$

giving the results $P^\alpha = 0.501$, $\mathbf{x}^\alpha = [0.2958,\ 0.0463,\ 0.6579]$ and $\mathbf{x}^\beta = [0.9677,\ 0.0167,\ 0.0156]$.

These new composition values are used again in step (b) until the desired convergence. These mole fraction will represent a point in the rectangular or triangular ternary phase diagram representation.

7. Results and Discussion

The ternary system, water(1)-ethanol(2)-ethyl acetate(3) will be used as a prototype model to illustrate the usage of the Rachford-Rice equation. The results in Table 1, at 70 °C and $p = 1$ atm, have been optimized to reproduce data in reference [11], using the previously published results [10] as an initial guess. The set of mole fractions $\mathbf{x}^\alpha = [0.2958,\ 0.0463,\ 0.6579]$, $\mathbf{x}^\beta = [0.9677,\ 0.0167,\ 0.0156]$, are compatible with $\boldsymbol{\gamma}^{\boldsymbol{\alpha}} = [3.2984,\ 0.5816,\ 1.2200]$ and $\boldsymbol{\gamma}^{\boldsymbol{\beta}} = [1.0083,\ 1.6128,\ 51.3854]$ for the NRTL equation, an useful result for testing part of a possible computer code.

As the system under analysis has 3 components, at a fixed temperature and pressure, one has, by the Gibbs

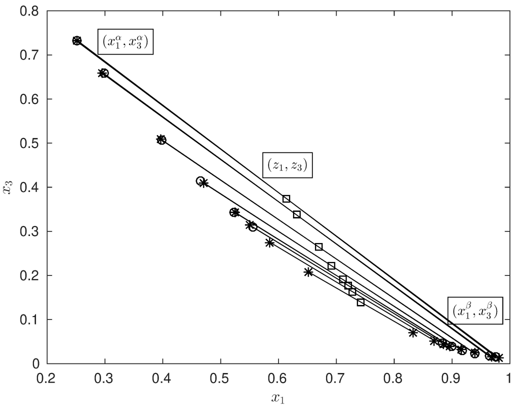


Figure 1: Rectangular diagram for the ternary system water(1)-ethanol(2)-ethyl acetate(3), at 70 °C. Experimental data (circles), calculated data (asterisks) and global composition (squares).

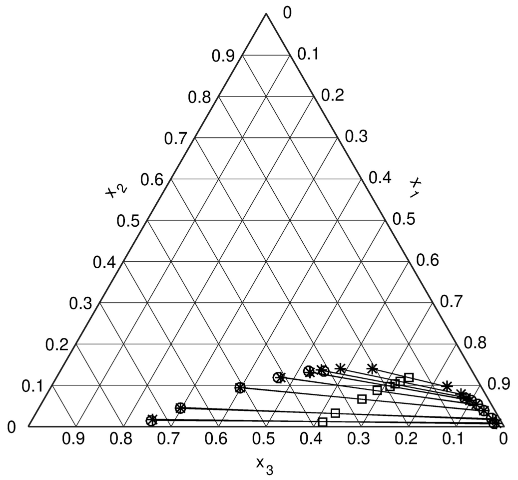


Figure 2: Triangular diagram for the ternary system water(1)-ethanol(2)-ethyl acetate(3), at 70 °C. Experimental data (circles), calculated data (asterisks) and global composition (squares).

phase rule [16], $F = 3 - P$. For the two-phase region ($P = 2$) there is one degree of freedom ($F = 1$), while two degrees of freedom ($F = 2$) are possible for the one-phase region ($P = 1$). Since P is at most two, two-dimensional diagrams (phase diagrams) can be used to represent the state of the system involving three components. Two equivalent, with two independent variables, are possible: one in which a third mole fraction is implicit (rectangular phase diagram) and one in which it appears explicitly (triangular phase diagram).

The rectangular and triangular phase diagrams for the ternary system under consideration are presented in Fig. 1 and 2, respectively. These diagrams show the results for equilibrium compositions, according to the algorithm explained in section 6 and for several global compositions.

As observed, there is a very good agreement when comparing calculated and experimental data with a root mean square error of 0.0027. Since the solution can converge to the trivial one (phases with the same composition) or to solutions that represent local minima of the Gibbs energy surface [17] it is important to have a reasonable initial condition. The same initial approximations $\mathbf{x}^\alpha = [0.1,\ 0.4,\ 0.5]$ and $\mathbf{x}^\beta = [0.950,\ 0.045,\ 0.005]$ proved to be satisfactory for all calculated results. It is important to mention that similar results were obtained by solving the eight-dimensional system, equation (11), indicating the overall simplicity of the Rachford-Rice equation. However, with the Rachford-Rice formulation one has to solve a problem with one independent variable, as in the equation (26).

A necessary condition to guarantee thermodynamic equilibrium is to achieve equality of activities (isoactivity), that is, $a_i^\alpha = a_i^\beta$, $i = 1, 2, 3$. The isoactivity of the results was evaluated, using the ratio a_i^α / a_i^β, whose ideal result is unity. For the calculated results, this quantity

Table 2: Calculated (cal) and experimental (exp) [11] phase compositions for the ternary system water(1)-ethanol(2)-ethyl acetate(3), at 70 °C and $p = 1\,\text{atm}$.

Tie line	z_1	z_2	z_3	x_1(exp)	x_2(exp)	x_3(exp)	x_1(cal)	x_2(cal)	x_3(cal)
1	0.6140	0.0120	0.3740	0.2520	0.0150	0.7330	0.2511	0.0177	0.7312
				0.9760	0.0090	0.0150	0.9814	0.0063	0.0123
2	0.6310	0.0315	0.3375	0.2980	0.0440	0.6580	0.2958	0.0463	0.6579
				0.9640	0.0190	0.0170	0.9677	0.0167	0.0156
3	0.6695	0.0660	0.2645	0.3990	0.0940	0.5070	0.3967	0.0950	0.5083
				0.9400	0.0380	0.0220	0.9385	0.0374	0.0241
4	0.6910	0.0865	0.2225	0.4650	0.1200	0.4150	0.4713	0.1198	0.4089
				0.9170	0.0530	0.0300	0.9151	0.0526	0.0323
5	0.7110	0.0980	0.1910	0.5230	0.1330	0.3440	0.5251	0.1319	0.3430
				0.8990	0.0630	0.0380	0.8955	0.0643	0.0401
6	0.7195	0.1025	0.1780	0.5550	0.1350	0.3100	0.5495	0.1358	0.3147
				0.8840	0.0700	0.0460	0.8856	0.0700	0.0444
7	0.7274	0.1091	0.1635	—	—	—	0.5852	0.1396	0.2753
				—	—	—	0.8695	0.0786	0.0518
8	0.7424	0.1182	0.1394	—	—	—	0.6515	0.1403	0.2081
				—	—	—	0.8333	0.0961	0.0706

was shown to have a maximum error of 1.73×10^{-6}, indicating not only the calculation accuracy but also the condition of equilibrium condition.

The results calculated in the present work and the experimental data [11] are presented in Table 2. The success in recovering these tie lines shows, again, the efficiency of the algorithm, even close to the critical point.

8. Conclusions

The Rachford-Rice method was presented for a three-component prototype system. The method is easy to implement, involving the solution of a second degree polynomial equation. The final solution is obtained iteractively.

The main advantage of the present method is its simplicity. In some systems, as in liquid-vapor equilibrium, the constant K_i does not depend on composition and the Rachford-Rice can be used to predict equilibrium composition with only one iteraction, independently of the number of components.

The most involved part of the method consists of establishing a suitable model for the activity coefficient. After this step, the computer code contains just over five commands. Using the NRTL model for the activity coefficient, the solution to the problem was established and the convergence obtained was within the experimental error, demonstrating the robustness of the algorithm. The Rachford-Rice equation, as presented here, is very simple to implement and suitable to teach ternary liquid-liquid equilibrium in undergraduated courses.

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