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CALCULATION OF LIQUID-VAPOUR AND LIQUID-LIQUID EQUILIBRIUM IN MULTICOMPONENT SYSTEMS USING CORRELATIONS OF EQUILIBRIUM DATA

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INTRODUCTION

Calculation of phase equilibria using algebraic correlations is based on empirical equations, whose parameters are obtained by optimization from a set of experimental equilibrium data. We propose logarithmic equations, based on the equation proposed by Marcilla et al. [1] for liquid-liquid equilibrium in quaternary systems including an inorganic salt, for the correlation of liquid-vapor and liquid-liquid equilibrium data.

The equation proposed by Marcilla et al. [1] was the following:

$$\log\left(\frac{y(2)}{y(3)}\right) = (a + b \cdot x(4)) + (c + d \cdot x(4)) \cdot \log\left(\frac{x(2)}{x(1)}\right) + (e + f \cdot x(4)) \cdot \left[\log\left(\frac{x(2)}{x(1)}\right)\right]^2 \quad (1)$$

The presence of logarithms and ratios of compositions in the equation prevents the introduction of equilibrium data in which some component has concentration equal to zero (binary and ternary equilibrium data). Consequently, and to correlate simultaneously all equilibrium data of the system, including binary and ternary data, it is necessary to modify the equation. A possibility is to add a positive and constant value (C) to the compositions, in mass or molar fractions, in order to avoid the infinite ratio of the compositions.

The optimization method, used to correlate simultaneously all the experimental equilibrium data of the systems considered in this work and to determine the parameters of the correlation, has been the optimization tool "Solver" of the calculation-sheet Excel 7.0 for Windows, using as objective function the square deviation between experimental and calculated data.

To obtain the composition (and the enthalpy in the case of the liquid-vapor equilibrium) of a phase in equilibrium with given known phase, it is necessary to combine (n-1) equations of this type for a system of n components.

LIQUID-VAPOUR EQUILIBRIUM CORRELATION

The modifications required for the application of the equation (1) are:

a) to consider the composition of all components of the system.

b) to introduce a quadratic term in the compositions.

c) to apply a variable change so that the liquid-vapor equilibrium of the ternary system could be treated as an hypothetical quaternary system. We have considered as fourth "composition" the value of a "modified enthalpy", besides the value of enthalpy used must be in the adequate units to have the same statistical weight, in the correlation, that the compositions.

PROPOSED MODEL

$$\log\left(\frac{\lambda(j)}{\lambda(i)}\right) = \mathrm{A} + \mathrm{B} \cdot \log\left(\frac{\eta(j)}{\eta(i)}\right) + \Phi \cdot \left(\log\left(\frac{\eta(j)}{\eta(i)}\right)\right)^2 \quad (2)$$

$$\mathrm{A} = a_1 + b_1 \cdot \eta(k) + c_1 \cdot \eta(l) + d_1 \cdot (\eta(k))^2 + e_1 \cdot (\eta(l))^2$$

$$\mathrm{B} = a_2 + b_2 \cdot \eta(k) + c_2 \cdot \eta(l) + d_2 \cdot (\eta(k))^2 + e_2 \cdot (\eta(l))^2$$

$$\Phi = a_3 + b_3 \cdot \eta(k) + c_3 \cdot \eta(l) + d_3 \cdot (\eta(k))^2 + e_3 \cdot (\eta(l))^2$$

$\eta(i), \eta(j), \eta(k), \eta(l)$: normalized coordinates of a point of the liquid phase:

$$\eta(1) = \frac{x(1)}{1+h} + C \qquad \eta(2) = \frac{x(2)}{1+h} + C \qquad \eta(3) = \frac{x(3)}{1+h} + C \qquad \eta(4) = \frac{h}{1+h} + C$$

$\lambda(i), \lambda(j), \lambda(k), \lambda(l)$: normalized coordinates of a point of the vapor phase:

$$\lambda(1) = \frac{y(1)}{1+H} + C \qquad \lambda(2) = \frac{y(2)}{1+H} + C \qquad \lambda(3) = \frac{y(3)}{1+H} + C \qquad \lambda(4) = \frac{H}{1+H} + C$$

LIQUID-LIQUID EQUILIBRIUM CORRELATION

For the correlation of ternary and quaternary tie lines in type I quaternary systems, the following equation is suggested:

PROPOSED MODEL

$$\log\left(\frac{\lambda(j)}{\lambda(i)}\right) = \alpha + \beta \cdot \log\left(\frac{\eta(2)}{\eta(1)}\right) + \phi \cdot \left(\log\left(\frac{\eta(2)}{\eta(1)}\right)\right)^2 \quad (3)$$

$$\alpha = a_1 + b_1 \cdot \left(\frac{\eta(4)}{\eta(2)}\right) + c_1 \cdot \left(\frac{\eta(4)}{\eta(2)}\right)^2$$

$$\beta = a_2 + b_2 \cdot \left(\frac{\eta(4)}{\eta(2)}\right) + c_2 \cdot \left(\frac{\eta(4)}{\eta(2)}\right)^2$$

$$\phi = a_3 + b_3 \cdot \left(\frac{\eta(4)}{\eta(2)}\right) + c_3 \cdot \left(\frac{\eta(4)}{\eta(2)}\right)^2$$

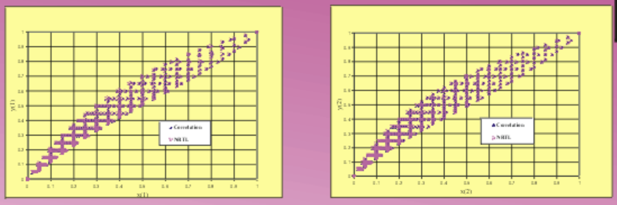
$\eta(i) = x(i) + C$: coordinates of a point of the aqueous phase.

$\lambda(i) = y(i) + C$: coordinates of a point of the organic phase.

RESULTS

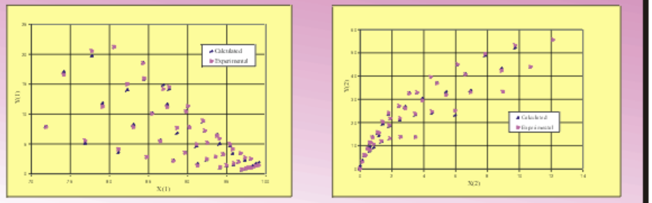
LIQUID-VAPOUR

Bencene-Cyclohexane-Toluene System



LIQUID-LIQUID

Water - Acetone - Chloroform - Acetic Acid



Nomenclature

$a_i, b_i, c_i, d_i, e_i, f_i$: Equilibrium correlation parameters of the model proposed.

C: Constant used in the variable change that permits to include in the correlation the binary and ternary equilibrium data.

h, H: Enthalpy of the liquid and vapor phases, respectively.

$x(i)$: Mole or mass fractions in the aqueous phase (liquid-liquid equilibrium) or liquid phase (liquid-vapor equilibrium).

$y(i)$: Mole or mass fractions in the organic phase (liquid-liquid equilibrium) or vapor phase (liquid-vapor equilibrium).

M: ratio of compositions x(2)/(x(2)+x(4)), being 2 and 4 the two solutes of the quaternary system, totally miscible with water.

Greek characters

A, B, Φ and α, β, φ: Parameters of the logarithmic equation used to correlate the liquid-vapor and the liquid-liquid equilibrium data, respectively.

$\lambda(i), \lambda(j), \lambda(k), \lambda(l)$: Normalized coordinates of the searched phase (vapor phase in the L-V equilibrium and organic phase in L-L equilibrium).

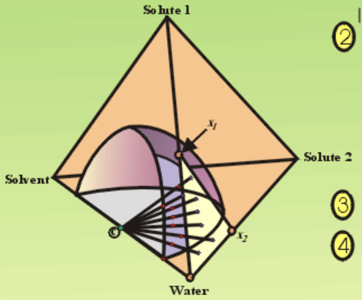
$\eta(i), \eta(j), \eta(k), \eta(l)$: Normalized coordinates of the known phase (liquid phase in the L-V equilibrium and aqueous phase in L-L equilibrium).

PROPOSED METHOD FOR THE CALCULATION OF THE TWO PHASES IN EQUILIBRIUM WITH A HETEROGENEUS LIQUID MIXTURE

The method involves the following steps:

- To suppose a composition for the aqueous phase.
- To calculate the composition of the organic phase in equilibrium with the aqueous phase supposed, using the correlations proposed.
- To check if the tie line defined by the aqueous phase supposed and its calculated conjugated organic phase contains the point representative of the initial heterogeneous mixture. Then, an iterative procedure starts, and it continues until the tie line containing the mixture point is found.

Liquid-liquid equilibrium introduces an additional complexity: NOT ALL COMPOSITIONS SUPPOSED FOR THE AQUEOUS PHASE EXIST AS EQUILIBRIUM PHASES OF THE QUATERNARY SYSTEM. To solve this difficulty a procedure to locate coherent compositions for the aqueous phases in type I quaternary systems is suggested:



① Obtain an equation representing the solubility surface, which contains all the equilibrium points of the system (correlation based on the Cruickshank projections):

$$x(3) + x(4) = (A' \cdot M + B') \cdot (x(1) + x(4)) + (C' \cdot M + D') \quad (4)$$

$$x(2) + x(4) = (A \cdot M^2 + B \cdot M + C) \cdot (x(1) + x(4))^2 + (D \cdot M^2 + E \cdot M + F) \cdot (x(1) + x(4)) + (G \cdot M^2 + H \cdot M + I) \quad (5)$$

To obtain a better correlation, only equilibrium points on the aqueous region of the solubility surface has been considered.

② Consider a triangle on the ternary plain Water - Solute 1 - Solute 2. The vertexes of this triangle have the following compositions:

- Vertex 1: Binary mixture whose concentration in solute 1 is equal to the highest concentration of this component in all the experimental aqueous equilibrium points.
- Vertex 2: Binary mixture whose concentration in solute 2 is equal to the highest concentration of this component in all the experimental aqueous equilibrium points
- Vertex 3: Pure water (water vertex of the tetrahedron).

③ Consider points inside of this triangle.

④ Each one of these points on the triangle is connected with the middle point of the binary tie line solvent-water. The intersection of these straight line with the solubility surface provides equilibrium points, which are on the aqueous region, which is the objective of this procedure.