DETERMINATION OF MULTICOMPONENT DIFFUSION COEFFICIENTS BY STUDYING HEAT AND MASS TRANSFER IN PARTIALLY SATURATED CAPILLARIES

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ABSTRACT

A study of simultaneous heat and mass transfer in partially saturated capillaries has been performed in order to determine the matrix of multicomponent diffusion coefficients in liquid phase. The literature provides a semi-empirical formula developed by Bandrowski and Kubaczka to calculate the matrix of multicomponent diffusion coefficients. The method separates the kinetic and thermodynamic contributions to mass transfer, and it contains an empirical exponent to improve the calculations. The present work attempts an estimation of the empirical exponent in a broad range of temperatures and liquid compositions by studying the redistribution of compositions in an unsaturated non-isothermal capillary, taking into consideration the non-ideality described by the matrix of thermodynamic factors. Two different ternary mixtures were tested at different temperature gradients and saturation degree. The results reveal that the method is effective since specific values of the empirical exponent that modifies the matrix of thermodynamic factors were obtained for each system. In addition, the exponent seems to be dependent on temperature.

INTRODUCTION

Multicomponent mass transfer has an important roll in most of the industrial unit operations, e.g. fractional distillation, absorption, extraction or high intensity drying of solid containing solvent mixtures. Mass transfer in multicomponet systems implies the knowledge of matrix **D** defined by the generalised Fick's Law.

The experimental measurement of elements of the matrix **D** demands considerable work. For instance, extending the binary diaphragm cell system described by Cussler [1] to a multicomponent system results in a large set of experiments. This fact is confirmed by Kosanovich and Cullinan [2]. If in addition, it were considered that the coefficients are strongly dependent on composition and temperature, the acquisition of experimental information demanded to follow processes with those characteristics would be very costly.

The predictive methods aimed to overcome this drawback by using the generalized Maxwell-Stefan formulation is an alternative approach to the multicomponent diffusion problem, which reduces to find methods to calculate the Maxwel-Stefan diffusion coefficients using a kinetic model and the matrix of thermodynamic factors from thermodynamic data. Cullinan and Kosanovich [3] have worked out a predictive method for determining the Maxwel-Stefan diffusion coefficients based on the theory of the ultimate volume. Bandrowski and Kubaczka [4] have developed a method, which gives better results. In extending the binary result to the multicomponent case, the authors found that the matrix of the thermodynamic factors should be corrected by using an empirical exponent to fit existing experimental data. Recently, several works on multicomponent mass transfer regarding the matrix of coefficients liquid diffusion have been done. Shapiro [5] and Medvedev et al [6] study the diffusion in terms of thermodynamic characteristics, such as molar density and internal energy. Unsula and Sunol [7] study multicomponent inter-phase diffusion at high pressure disregarding modifications on the matrix of thermodynamic factor.

The present work is focused to determine Bandrowski and Kubaczka's empirical exponent from the liquid composition redistribution produced in an unsaturated capillary exposed to a stationary temperature gradient. This measurement method will provide a contribution aimed to elucidate the transport parameters in drying of solids containing multicomponent liquid mixtures.

NOMENCLATURE

A matrix defined by Eq. (9)
b vector defined by Eq. (10)
B matrix with elements defined by Eqs. (3) and (4) (s/m^2)
c concentration ($kmol/m^3$)
D matrix of multicomponent diffusion coefficients (m^2/s)
$Đ$ Maxwell-Stefan diffusion coefficient (m^2/s)
n number of components (-)
s saturation (-)
T temperature (K)
u liquid content (m^3/m^3)
w molar fraction (kmol/kmol)
W matrix with elements defined by Eq. (11) (-)
x molar fraction in liquid phase (kmol/kmol)
x vector of molar fractions in liquid phase (kmol/kmol)
y molar fraction in gas phase (kmol/kmol)
y vector of molar fractions in gas phase (kmol/kmol)
z length coordinate (m)

Greek Letters
γ activity coefficient (-)
Γ matrix of thermodynamic factors with elements defined in Eq.(5) (-)
δ Kronecker delta (-)
ε solid porosity (-)
ζ exponent of the matrix of thermodynamic factors (-)

Subscripts
g denotes gas phase
ij binary, position in matrix
ik binary, position in matrix
l denotes liquid phase

Superscripts
T transposition
' dimension reduction

MULTICOMPONENT DIFFUSION THEORY

Fick's generalized law for multicomponent diffusion is one of the approaches used to account for these interactions. It is based on the assumption of linearity between the diffusion fluxes and the molar fraction gradients:

$$\mathbf{J} = -c_l\,\mathbf{D}_l\,\frac{\partial \mathbf{x}}{\partial z} \tag{1}$$

where **J** is the vector of diffusion fluxes, c is the concentration, subscript l denotes liquid phase, **x** is the vector of liquid molar fraction, and z is the unidirectional coordinate length. **D** is the matrix of multicomponent diffusion coefficients expressed in compact matrix notation as follows [8]:

$$\mathbf{D}_l = \mathbf{B}^{-1}\mathbf{\Gamma} \tag{2}$$

with the elements of **B** and $\mathbf{\Gamma}$ defined by:

$$B_{ii} = \frac{w_i}{Đ_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n}\frac{w_k}{Đ_{ik}} \qquad i = 1,2,\ldots n-1 \tag{3}$$

$$B_{ij} = -w_i\left(\frac{1}{Đ_{ij}} - \frac{1}{Đ_{in}}\right) \qquad i \neq j = 1,2\ldots n-1 \tag{4}$$

$$\Gamma_{ij} = \delta_{ij} + \frac{w_i}{w_j}\frac{\partial\ln\gamma_i}{\partial\ln\gamma_j} \qquad i,j = 1,2,\ldots n-1 \tag{5}$$

where $w = x$ (liquid molar fraction), $Đ_{ij}$ are the multicomponent Maxwell-Stefan diffusion coefficients, $\mathbf{\Gamma}$ is the matrix of thermodynamic factors, γ_i and γ_j are the activity coefficients, n is the number of components in the mixture, and δ_{ij} is the Kronecker delta (1 if $i = j$, 0 if $i \neq j$).

For gases, the matrix of diffusion coefficients reduces to:

$$\mathbf{D}_g = \mathbf{B}^{-1} \tag{6}$$

with $w = y$ (gas molar fraction) in equations (3) and (4).

Values of $Đ_{ij}$ have been calculated extending expressions given for binary systems. For instance, Hayduk-Minhas' model, reported by Poling et al [9], has been commonly used for dilute mixtures. Vignes' model has been consistently used first in generalised form for multicomponent systems by Cullinan [10] and much later by Kooijman and Taylor [11]. For gases, Fuller's model, also reported by Poling et al [9] is a suitable one.

Bandrowski and Kubaczka [4] concluded that for more reliable results on predicting diffusivities in multicomponent liquid systems, the thermodynamic matrix should be exponentially modified, so that Eq. (2) becomes:

$$\mathbf{D}_l = \mathbf{B}^{-1}\mathbf{\Gamma}^{\zeta} \tag{7}$$

MASS TRANSFER IN A SEALED CAPILLARY EXPOSED TO A TEMPERATURE GRADIENT

Martínez [12] found that the literature reports liquid composition redistributions caused by temperature gradients. Considering an unsaturated porous solid as a simple straight capillary sealed in its extremes shown in Fig. 1, the mechanisms of heat and mass transfer can be analysed in a very simplified arrangement of the phases.
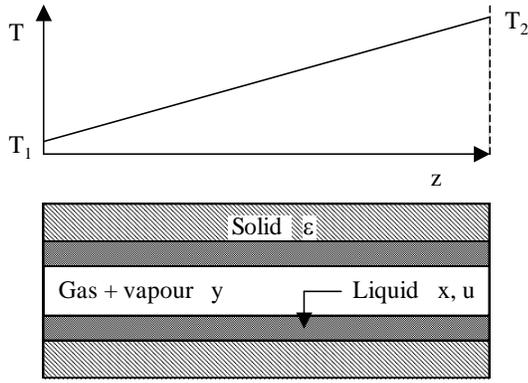
Figure 1: *Unsaturated capillary exposed to a temperature gradient.*

If the extremes of the capillary are sealed for mass transfer and a known steady state temperature gradient is imposed parallel to the phases, the net flow at every position along the capillary is zero. Written as a function of the saturation of the pores, $s = u \square \varepsilon$ that leads to the following expression:

$$\mathbf{A}\frac{d\mathbf{x}}{dz} = \mathbf{b}\frac{dT}{dz} \qquad (8)$$

where $\mathbf{x}$ is the vector of liquid composition, T is the absolute temperature and z the capillary length position. The matrix $\mathbf{A}$ and vector $\mathbf{b}$ for a system containing an inert in each phase are:

$$\mathbf{A} = \{1-s\}c_g \mathbf{YD}_g \frac{\partial \mathbf{y}}{\partial \mathbf{x}} - sc_l \mathbf{XD}_l \qquad (9)$$

$$\mathbf{b} = \{1-s\}c_g \mathbf{YD}_g \frac{\partial \mathbf{y}}{\partial T} \qquad (10)$$

where $\mathbf{D}_g$ and $\mathbf{D}_l$ are given by equations. (6) and (7) respectively; $\partial \mathbf{y}/\partial \mathbf{x}$ is the matrix of derivative of vector $\mathbf{y}$ (gas molar fraction) with respect to vector $\mathbf{x}$ (liquid molar fraction); $\partial \mathbf{y}/\partial T$ is the vector of derivative of vector $\mathbf{y}$ with respect to the temperature. $\mathbf{X}$ and $\mathbf{Y}$ are defined as matrix $\mathbf{W}$ with elements:

$$W_{ik} = \frac{w_i}{w_n} + \delta_{ik} \qquad\qquad i,k = 1,2,\ldots n\text{-}1 \qquad (11)$$

If all components of the liquid phase are volatile, matrix $\mathbf{A}$ and vector $\mathbf{b}$ are:

$$\mathbf{A} = \{1-s\}c_g\left\{\left(\mathbf{YD}_g \frac{\partial \mathbf{y}}{\partial \mathbf{x}}'\right)_{n-1} - \frac{1}{y_{n+1}}\mathbf{x}_{n-1}\mathbf{1}^T \mathbf{D}_g \frac{\partial \mathbf{y}}{\partial \mathbf{x}}'\right\} +$$

$$+ sc_l \mathbf{D}_l \qquad (12)$$

$$\mathbf{b} = \{1-s\}c_g\left\{-\left(\mathbf{YD}_g \frac{\partial \mathbf{y}}{\partial T}\right)_{n-1} + \frac{1}{y_{n+1}}\mathbf{x}_{n-1}\mathbf{1}^T \mathbf{D}_g \frac{\partial \mathbf{y}}{\partial T}\right\} \qquad (13)$$

The apostrophe in the matrix $\partial \mathbf{y}/\partial \mathbf{x}$ in Eq (12) implies a reduction of the matrix dimension to *n-1* columns.

Eq. (8) reveals that if a temperature gradient is applied between the extremes of the sealed capillary, a redistribution of liquid composition proportional to the temperature gradient will result. If the temperature gradient is a known function of z:

$$\frac{dT}{dz} = g(z) \qquad (14)$$

The ordinary set of differential equations (8) and (14) may be integrated in any interval to determine the steady state redistribution of liquid composition.

EXPERIMENTAL WORK

Experimental Set-up
The capillary system for measuring temperature and concentrations profiles is shown in Fig. 1 and described as follow.

A horizontal and isolated capillary tube of 1.3-cm internal diameter and 12.5-cm length contains the testing ternary mixture. Heating and cooling chambers are plugged to each extreme of the tube in order to provoke a longitudinal temperature gradient. Such chambers are fed with hot and cold water respectively from isothermal baths. Thermocouples are set along the tube every 15-mm to control and record the temperature profile up to the steady state. In addition, sample points are located along the tube corresponding to each thermocouple. Samples taken from these points are analysed to obtain the local concentrations, which define the liquid distribution profile once the steady state is reached.

Experiment
The ternary mixture studied was loaded into the capillary tube up to certain saturation degree. In order to impose a range of temperature, both heating and cooling chambers were maintained at constant temperature by circulating water flows from the hot and cold thermal baths respectively.

The temperature variation was monitored on a computer until reaching the steady state; then, the steady state profile was recorded. Samples were taken from each sample point at the same time using capillary syringes. Table 1 shows the multicomponent systems experimentally tested and the working conditions.
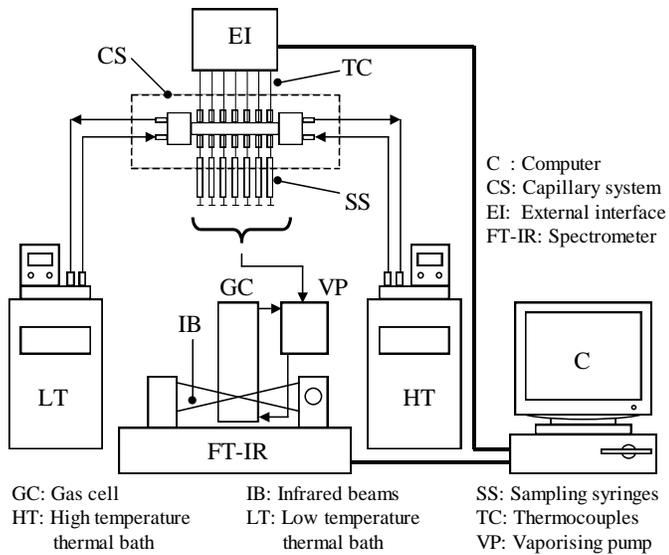
Figure 2: *Experimental set-up: Capillary tube and peripheries.*

C : Computer
CS: Capillary system
EI: External interface
FT-IR: Spectrometer

GC: Gas cell
HT: High temperature thermal bath
IB: Infrared beams
LT: Low temperature thermal bath
SS: Sampling syringes
TC: Thermocouples
VP: Vaporising pump

The sample analysis was performed in the FT-IR spectrophotometer, which is calibrated with known spectra of the pure compounds of each tested ternary mixture. Mixture spectra were taken while the samples contained in each syringe were injected through a vaporising pump in such a way that the mixture vapour circulated in closed loop passing through the spectrophotometer gas cell. Finally, both temperature and concentration at steady state were plotted against the tube length. The resulting profiles were compared with the theoretical liquid distribution generated by solving the set of differential equations (8) and (14). The optimisation stopped as the exponent acting on the diffusion matrix was adjusted.

Table 1: *Experimental conditions.*

System	Imposed range of temperature (K)	Sat. (-)
Ethanol-MEK*-toluene	278.15 – 328.15	0.95 0.60
	278.15 – 348.15	0.95 0.60
Water-ethanol-acetone	278.15 – 328.15	0.95 0.60
	278.15 – 348.15	0.95 0.60

* MEK: Methylethylketone

RESULTS

Solving the ordinary set of differential equations (8) and (14), while simultaneously comparing with experimental data of liquid composition in a capillary tube, values of the empirical exponent that acts over the matrix of thermodynamic factors were calculated.

The ternary vapour-liquid equilibrium was computed using Wilson equations with constants from Gmehling and Onken [13]. Other physical properties of the mixtures (e.g. liquid and gas binary diffusivities) were calculated according to methods reported by Poling et al [9].

Figures 3 and 4 show the final adjustment reached for the two systems. Table 2 includes the results for the two multicomponent systems tested.
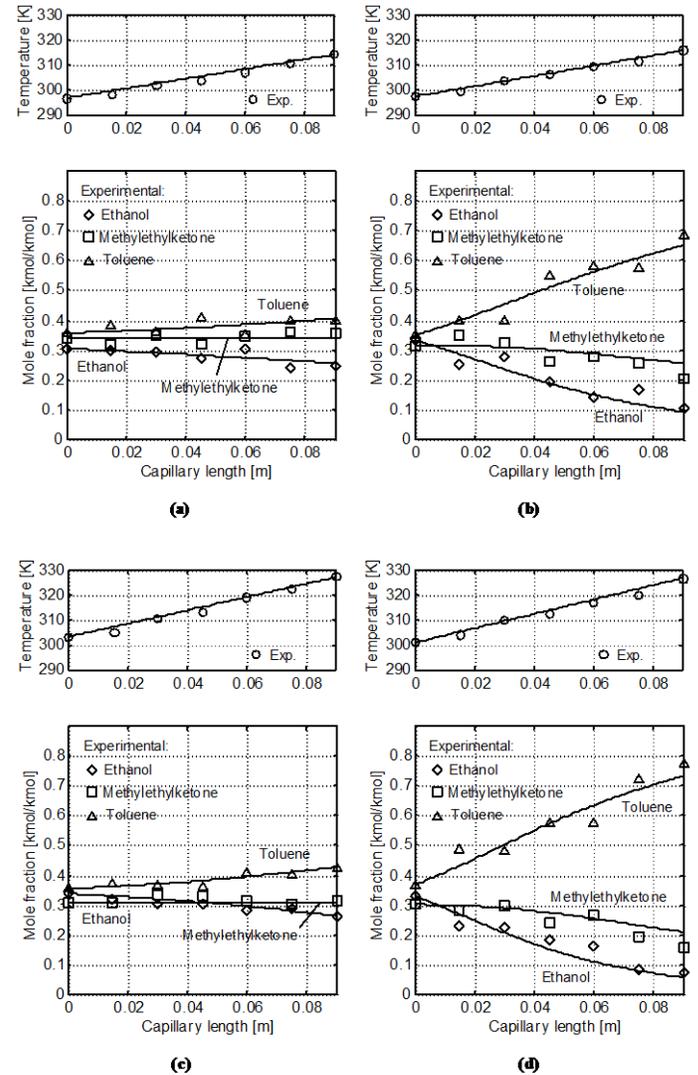

(a) (b) (c) (d)

Figure 3: *Molar fraction distribution of the ternary mixture ethanol-methylethylketone-toluene (theoretical distribution defined by solid lines): a) temperature range of 278.15 –328.15 K and s = 0.95, b) temperature range of 278.15 –328.15 K and s = 0.60, c) temperature range of 278.15 –348.15 K and s = 0.95, d) temperature range of 278.15 –348.15 K and s = 0.60.*

The saturation degree exerts a significant influence on the liquid distribution since the relative importance of the flow in each phase is modified. At lower saturation, the concentration gradients in liquid phase are more pronounced, i.e. toluene in Fig. 3 and water in Fig. 4.
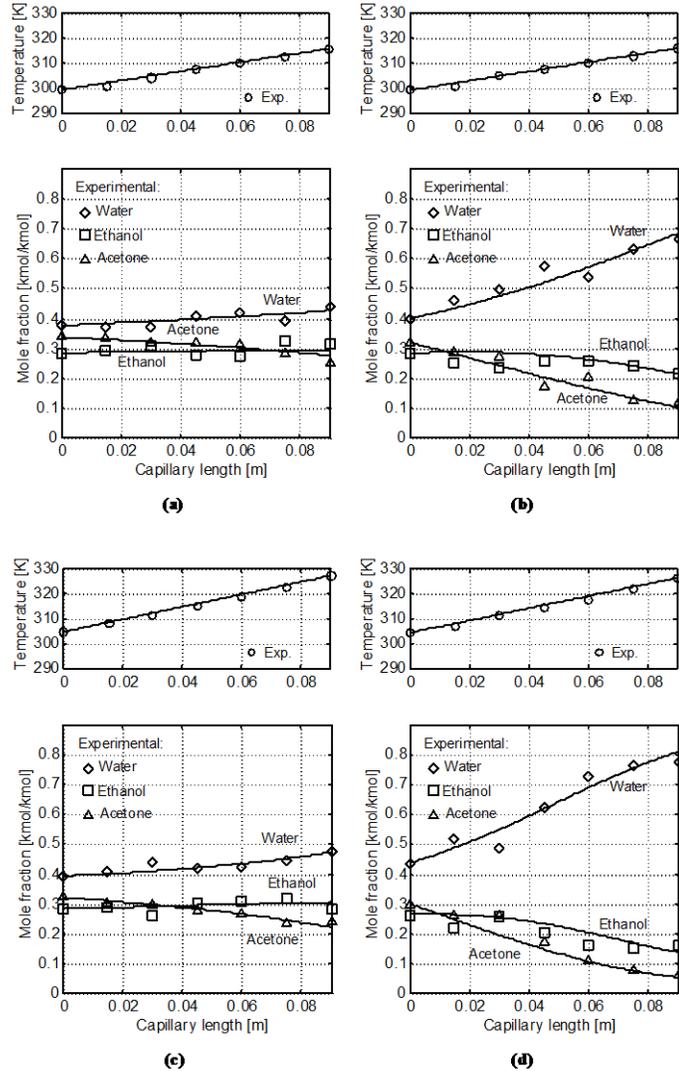

Figure 4: *Molar fraction distribution of the ternary mixture water-ethanol-acetone (theoretical distribution defined by solid lines): a) temperature range of 278.15 –328.15 K and s = 0.95, b) temperature range of 278.15 –328.15 K and s = 0.60, c) temperature range of 278.15 –348.15 K and s = 0.95, d) temperature range of 278.15 –348.15 K and s = 0.60.*

Temperature influences on the matrix of multicomponent diffusion coefficients since both the Maxwell-Stefan coefficients and thermodynamic factors are directly affected through the viscosity and the activity coefficient respectively. However, the results also reveal that the exponent ζ seems to be function of temperature (see Table 2). Since the values of ζ are

close each other under similar temperature gradients, mean values are reported in Table 2 as fixed valid values. With more experimental data, an explicit formula for the dependence on temperature could be developed.

Table 2: *Resulting values of exponent ζ from the adjustment of the theoretical model with experimental data.*

System	Referred to Figure	Exponent ζ (-)	Mean $\bar{\zeta}$ (-)
Ethanol-MEK*-toluene	3a	0.7882	0.7354
	3b	0.6826	
	3c	0.4049	0.3379
	3d	0.2709	
Water-ethanol-acetone	4a	0.5834	0.5403
	4b	0.4972	
	4c	0.3323	0.3131
	4d	0.2939	

* MEK: Methylethylketone

CONCLUSION

The redistribution of liquid compositions in an unsaturated capillary containing a multicomponent liquid mixture and exposed to a temperature gradient has been verified.

The concentration gradients in liquid phase are more pronounced at low saturation. Consequently, further experiments should be performed at low saturation to obtain noticeable differences in concentration.

The method to calculate the empirical exponent that modifies the matrix of thermodynamic factors is proved to be effective. Values of ζ for the two ternary systems studied show good agreement between the theoretical liquid distribution and experimental data. Arithmetical mean values obtained from exponents calculated under similar temperature gradients are satisfying.

The empirical exponent that modifies the matrix of thermodynamic factors is not constant and seems to depend on temperature. Additional experimental work is needed to develop an expression that provides a function with the temperature in a broader range.

The study of the steady-state composition gradients induced in a sealed capillary resulting in the estimation of the exponent ζ and, therefore, a more accurate approach of the matrix of the liquid diffusion coefficients is a very useful tool for studying the transport parameters involved in multicomponent mass transfer in porous solids.

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