ESTEC/CONTRACT 8125/88/NL/FG
PRF 141315

Modelling of the MELiSSA artificial ecosystem

Gas-liquid equilibrium modelling for VFA and ammonia

- Vapor pressure of VFA and ammonia
- Influence of pH and temperature
- Prediction of activity coefficients at infinite dilution in water and gas-liquid equilibrium model at infinite dilution conditions

TECHNICAL NOTE 23.1

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January 1995

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T.N. 23.1: Modelling of the MELiSSA artificial ecosystem
GAS-LIQUID MODEL FOR VFA AND AMMONIA

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INTRODUCTION

A gas-liquid equilibrium model has been established in order to build a flowsheet of the MELiSSA loop including gas and liquid streams. The previous model described in the Technical note 17.1 (1) was based upon the calculation of partition coefficients (k_i) for five compounds: water, dioxygen, carbon dioxide, dinitrogen and dihydrogen.

The simulations of the loop performed with this model have led to the following conclusions:

- a control of the liquid streams must be introduced in the flowsheet design. This control must be applied on each biological compartment through a water management system in order to control the concentrations of the compounds in the streams.

- other components have to be considered. These compounds are Volatile Fatty Acids (acetate, butyrate, valerate, isovalerate....), lactic acid and ammonia.

The purpose of this note is to extend the work presented in the T.N. 17.1 to the above components and to propose a more reliable model of gas-liquid equilibrium valid for all compounds involved in the MELiSSA loop simulations.

The gas-liquid equilibrium model give the partition of a compound between the gas and the liquid phases assuming a perfect equilibrium. It must be kept in mind that such an equilibrium is not necessary reached in bioreactors where dynamics (transfer limitation, reactor design) and growth kinetics (respiration) play an important role. But it is important to note that it is necessary to determine and to predict the equilibrium concentrations, which are the start point for the modelling the transfer between liquid and gas phases.

I- GAS-LIQUID EQUILIBRIUM, DYNAMICS AND KINETICS

The transport of a compound from the gas to the liquid phase (or from the liquid to the gas phase) is an important aspect which must be considered for the design of a bioreactor. In the case of aerobic processes, the mechanism of oxygen transfer for the bulk of the gas phase into the bulk of the liquid suspension of single cell organisms is controlled by the liquid phase mass transfer resistance (2). This process is schematically illustrated in figure 1.

At the gas-liquid interface, there is a thermodynamic equilibrium between gas and liquid phases. In the bulk of the liquid, the concentrations of the compounds which are exchanged between gas and liquid are different. In the case of a transfer from the gas phase to the liquid phase (case of oxygen for aerobic processes) the concentration in the bulk liquid is lower than the equilibrium concentration, inducing a concentration gradient which is the driving force for diffusion from the gas to the liquid (figure 1). in the opposite case, *i.e.* production of a volatile compound inside the liquid phase and transfer to the gas phase (case of CO_2 and more generally of the volatile metabolites), the concentrations in the liquid are greater than the equilibrium concentration.

Generally speaking, the microorganisms are sensitive to the bulk concentrations which can reach limiting values in the case of consumption or inhibiting values in the case of the production of volatile metabolites. These bulk concentrations depend on the equilibrium concentrations and on the intensity of the transfer *i.e.* the gas-liquid transfer kinetics.

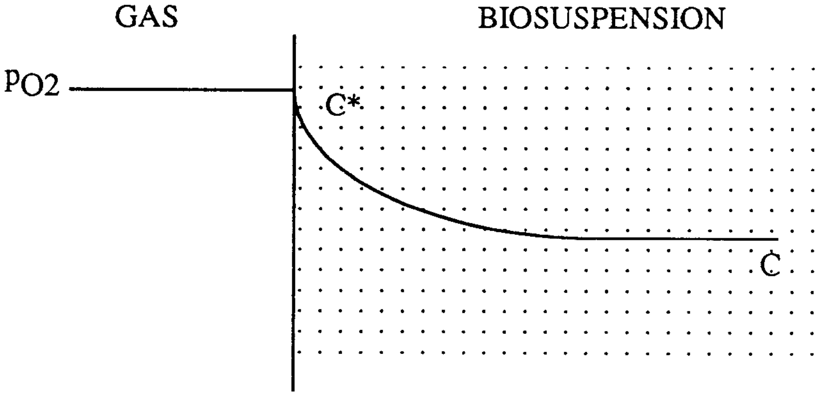


Figure 1: Oxygen profiles for transport from the inside of the gas phase into the bulk of the biosuspension

The intensity of the transfer depends on the driving forces i.e. the difference between the equilibrium concentrations and the bulk concentrations, and on the mass transfer coefficients which are under control of physical parameters such as diffusion coefficients and the interfacial area. Mathematically, the exchange phenomenum between gas and liquid phases is represented by the non-steady state balance of compound i in the liquid phase. For a perfectly mixed situation of the liquid, the balance takes the following form:

$$\frac{dC_i}{dt} = K_La|_i \, (C_i^* - C_i) + r_i$$

where C_i is the concentration of the dissolved gas i

C_i^* is the concentration of compound i at equilibrium with the gas composition

r_i is the production rate of i by a microorganism ($r_i > 0$ is a production, $r_i < 0$ is a consumption)

$K_La|_i$ is the volumetric transfer coefficient of compound i in liquid phase.

Generally, r_i is a function of the concentration in the bulk liquid C_i and the form of this function is determined by the study of the microbial kinetics.

It must be noted that $K_La|_i$ is a key parameter for characterising the transfer of the compound i. It is the product of the gas transfer coefficient (K_L) and of the interfacial area per unit of dispersion (a). These two parameters depend on the reactor design and working conditions.

In the case of an aerated stirred reactor HO et al. (3) determined for the oxygen transfer:

$$a = \frac{6H}{d_m}$$

d_m=Sauter bubbles mean diameter
H=gas hold-up

and

$$K_L \propto D_L^{\frac{2}{3}}$$

D_L=gas diffusion coefficient in the liquid phase.

If the value of the gas-liquid volumetric transfer coefficient is high ($K_La|_i >> r_i/C_i^*$), the difference (C_i^*-C_i) approaches zero such as the bulk concentration C_i can be approximated by C_i^*. At the opposite case, if $K_La|_i$ is low, C_i approaches zero value and r_i is approximated by the product $K_La|_i$ C_i^*.

This latter case corresponds to a transfer limitation and it must be kept in mind that the biological kinetics is under control of the physical parameters $K_La|_i$ and C_i^*. Therefore, it must be concluded that when compounds are exchanged between the gas and the liquid phases, a proper modelling of the process requires the knowledge of the following points:

- gas-liquid volumetric transfer coefficients which further implies the design of the fermenters technology;
- equilibrium concentrations which are determined from thermodynamical considerations (see below)
- biological kinetics which can be approached by stoichiometric models.

The result can be a biological controlled kinetics, a mass transfer controlled kinetics or any other intermediate case of coupling between mass transfer and biological kinetics which must be treated by integration of liquid phase balance equation.

It must be noted that additional mass transfer resistances such as liquid-solid mass transfer and intraparticle diffusion, may be important for larger microbial conglomerates (biofilms, pellets, immobilised biomass).

The gas-liquid equilibrium description then depends on the reactor design and working conditions (determination of K_La), on the microorganism metabolism (determination of r_i from the growth kinetics and the growth yield *i.e.* the stoichiometric description of the growth) and on the calculation of the gradient (C_i^*-C_i) in the liquid phase (figure 1).

The previous gas-liquid equilibrium model find its place in this description of the gasses behaviours by the determination of liquid concentrations at the equilibrium *i.e.* the determination the values of C_i^*., what lead to the determination of the gradient.

This technical note is aimed to the thermodynamic description of the equilibrium concentration Ci* for the different compounds which are involved in the MELiSSA loop.

II - EXTEND OF PREVIOUS MODEL FOR GAS-LIQUID EQUILIBRIUM TO VFA AND AMMONIA

For the present simulation design of the MELiSSA loop the sole thermodynamic constraint taken into account is the gas-liquid equilibrium. An ideal behaviour of the liquid and gas phases is assumed and a flash module from the modules library of the ProSim steady state simulator is used after a reactor module which simulates the biological reaction in a compartment (figure 2).
The aim of a flash module is to calculate the composition of the different phases (namely gas and liquid phases) knowing the total composition, temperature and total pressure.

The model is based upon the determination of the partition of a compound i between the gas and the liquid phases. The partition coefficient k_i is calculated as follows:

$$k_i = \frac{y_i}{x_i}$$

x_i : molar fraction of the compound i in the liquid phase
y_i : molar fraction of the compound i in the gas phase

The partition coefficient of a compound depends on temperature, on pressure and on the concentrations of all dissolved compounds. The physical limitations such as transfer limitations are not taken into account in flash calculations.

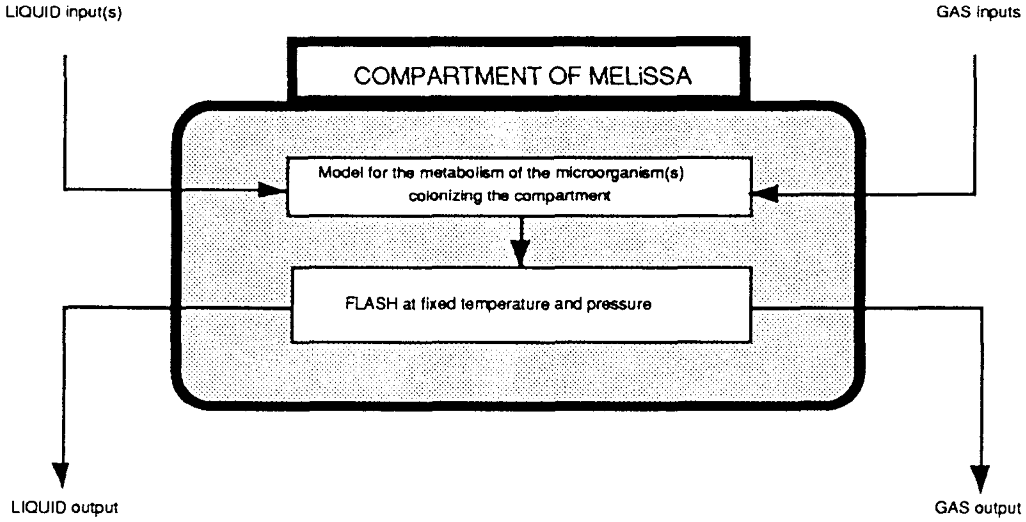


Figure 2: representation of a compartment for simulations

At the present time the sole parameters taken into account in the partition coefficient calculations are temperature and pH, and an ideal behaviour is supposed for the others. Thus the gas-liquid equilibrium model result in the calculation of $k_i(T,pH)$ for the compounds involved in the MELiSSA loop.

2.1 - Previous results: $k_i(T,pH)$ for O_2, CO_2, H_2, N_2 and water

From the solubility (x_i) of the compound in water for O_2, CO_2, H_2 and N_2, expressed as a function of temperature, and from the ANTOINE law for the vapor pressure of water, equations for $k_i(T)$ of these five compounds have been deduced, assuming a total pressure of 1 atm (1).

These equations have the form

$$\ln x_i = A' + \frac{B'}{T^*} + C' \ln T^*$$

and

$$T^* = \frac{T}{100}$$

where T is the temperature in Kelvin.

For dissolved carbon dioxide, a similar correlation is proposed:

$$\ln x_i = A' + \frac{B'}{T} + C' \ln T + D'.T$$

The equation constants, the standard deviation for $\ln x_i$ and the temperature range over which the equation applies are given in table 1 for dinitrogen, dioxygen, dihydrogen and carbon dioxide. Considering the previous assumptions, the solubility of a gas i under a partial pressure of 1 atm is characterised by the partition coefficient k_i calculated as follows:

$$k_i = \frac{1}{x_i}$$

Table 1: constants for the determination of gas solubilities

Compound	A'	B' (K)	C'	D' (K^{-1})	Std. deviation	Temp. range (K)
Hydrogen	-48.1611	55,2845	16,8893		+/- 0.54%	273.15-353,15
Oxygen	-66.7354	87.4726	24.4726		+/- 0.36%	273.15-348.15
Dinitrogen	-67.3877	86.3213	24.7981		+/- 0.72%	273.15-348.15
Carbon dioxide	-159.854	8741.68	21.6694	$-1.103\ 10^{-3}$	+/-0.54%	273.15-353.15

The vapor pressure of water, P^o_w, is satisfactorily expressed through the ANTOINE law as a function of temperature:

$$\ln P^o_w = A - \frac{B}{C + T}$$

where T is in Kelvin,
P^o_w is in mm Hg,
A=18.3036
B=3816.44 (K)
C=-46.13 (K)
the temperature range is 284 to 441 K

Considering that the activity of water remains equal to 1, k_w, the partition coefficient of water, is defined as:

$$k_w = \frac{P_w^o}{P_t} = y_w$$

It must be kept in mind that the previous correlations enable to calculate the k_i's as functions of temperature at the reference atmospheric partial pressure for all the dissolved species. At present time, it is supposed that all gas streams in MELiSSA remain at 1 atm., which prevents to recalculate the k_i's as a function of pressure by:

$$k_i(P) = \frac{k_i(1 \text{ atm.})}{P_t}$$

The effect of pH is taken into account only for carbon dioxide and no pH effects are supposed for the other compounds O_2, N_2, H_2 and water. Thus, instead of $k_{CO2}(T)$, $k^{ap}_{CO2}(T,pH)$ is considered as the carbon dioxide partition coefficient in the model for the gas-liquid equilibrium.

$$k^{ap}_{CO_2}(T,pH) = \frac{\left(k_{CO_2}(T) + y_{CO_2}\,\xi(T,pH)\right)}{1+\xi(T,pH)}$$

where

$$\xi(T,pH) = \frac{K_1(T)}{10^{-pH}}\left(1 + \frac{K_3(T)}{10^{-pH}}\right)$$

$$K_1(T) = \frac{[HCO_3^-].[H^+]}{[CO_2]}$$

$$K_3(T) = \frac{[CO_3^{2-}].[H^+]}{[HCO_3^-]}$$

The concentration of CO_2 obtained in the liquid phase using this model is in fact the value of the total carbon dioxide dissolved (CO_2, HCO_3^- and CO_3^{2-}).

2.2 - Determination of $k_i(T)$ for VFA and ammonia

In order to complete the gas-liquid equilibrium model for the MELiSSA loop simulation, all the compounds involved in the simulation (see table 2) must be considered.

Table 2: Compounds and possible compounds involved in the MELiSSA loop

Compounds involved presently	k_i determination
Water	Yes
Faeces	Unnecessary
Urea	Unnecessary
Carbon dioxide	Yes
Dioxygen	Yes
Dinitrogen	Yes
Dihydrogen	Yes
Nitrate	Unnecessary
Ammonia	To determine
Spirulina biomass	Unnecessary
Rhodobacteraceae biomass	Unnecessary
Glucose	Unnecessary
Palmitic acid	Unnecessary
Butyric acid	To determine
Acetic acid	To determine
New compounds to include	
Isobutyric acid	To determine
Isovaleric acid	To determine
Lactic acid	To determine
Ethanol	Not presently considered
Methane	Not presently considered
Caproic acid	To determine
Valeric acid	To determine
Isocaproic acid	To determine
Propionic acid	To determine
H_2SO_4	Not presently considered
H_3PO_4	Not presently considered
HCl (pH regulation)	Not presently considered
NaOH (pH regulation)	Not presently considered

2.2.1 - Ammonia

The vapor pressure of ammonia (P^o_{NH3}) is satisfactorily expressed through the ANTOINE law as a function of temperature of which equation constants are based upon published vapour pressure data (4 - 5)

$$\ln P^o_{NH_3} = A - \frac{B}{C + T}$$

where T is in Kelvin,
P^o_{NH3} is in mm Hg,
A=17.8693
B=2584.9 (K)
C=-9.49 (K)
the temperature range is 240 to 371 K

For the same ANTOINE law other parameters values can be found in the ProPhy thermodynamic library

T is in Kelvin,
P^o_{NH3} is in mm Hg,
A=16.83
B=2133 (K)
C=-32.98 (K)
the temperature range is 179 to 261 K

The difference between the two sets of parameters can be a consequence of the different ranges of temperature. The first set is more useful because the temperature range is in better agreement with the MELiSSA working conditions than the temperature range of the second set of parameters.

2.2.2 - Volatile Fatty Acid

Volatile Fatty Acids (VFA) are the products of the consumer wastes degradation by compartment I. Nine major organic acids are attempted in the outputs of the liquefying compartment (6):

Acetic acid
Butyric acid
Isobutyric acid
Valeric acid
Isovaleric acid
Caproic acid
Isocaproic acid
Propionic acid
Lactic acid

Methane and ethanol productions are attempted too, but at the present time these compounds are not considered.

Although data giving the vapour pressure of the 9 VFA versus temperature are available in the literature (7), no correlations between vapour pressure (or solubility) and temperature can been found; thus, fitted correlations must be established from these data (reported in table 3 and figure 3).

Table 3: Vapor pressures of organic acids up to 1 atm

	Pressure mm Hg									
	1	5	10	20	40	60	100	200	400	760
	Temperature °C									
Acetic acid	-17.2	6.3	17.5	29.9	43.0	51.7	63.0	80.0	99.0	118.1
Butyric acid	25.5	49.8	61.5	74.0	88.0	96.5	108.0	125.5	144.5	163.5
Isobutyric acid	14.7	39.3	51.2	64.0	77.8	86.3	98.0	115.8	134.5	154.5
Lactic acid	9.6	33.7	45.3	58.1	72.3	81.8	93.7	111.8	131.7	151.5
Propionic acid	4.6	28.0	39.7	52.0	65.8	74.1	85.8	102.5	122.0	141.1
Valeric acid	42.2	67.7	79.8	93.1	107.8	116.6	128.3	146.0	165.0	184.4
Isovaleric acid	34.5	59.6	71.3	84.0	98.0	107.3	118.9	136.2	155.2	175.1
Caproic acid	71.4	89.5	99.5	111.8	125.0	133.3	144.0	160.8	181.0	202.0
Isocaproic acid	66.2	83.0	94.0	107.0	120.4	129.6	141.4	158.3	181.0	207.0

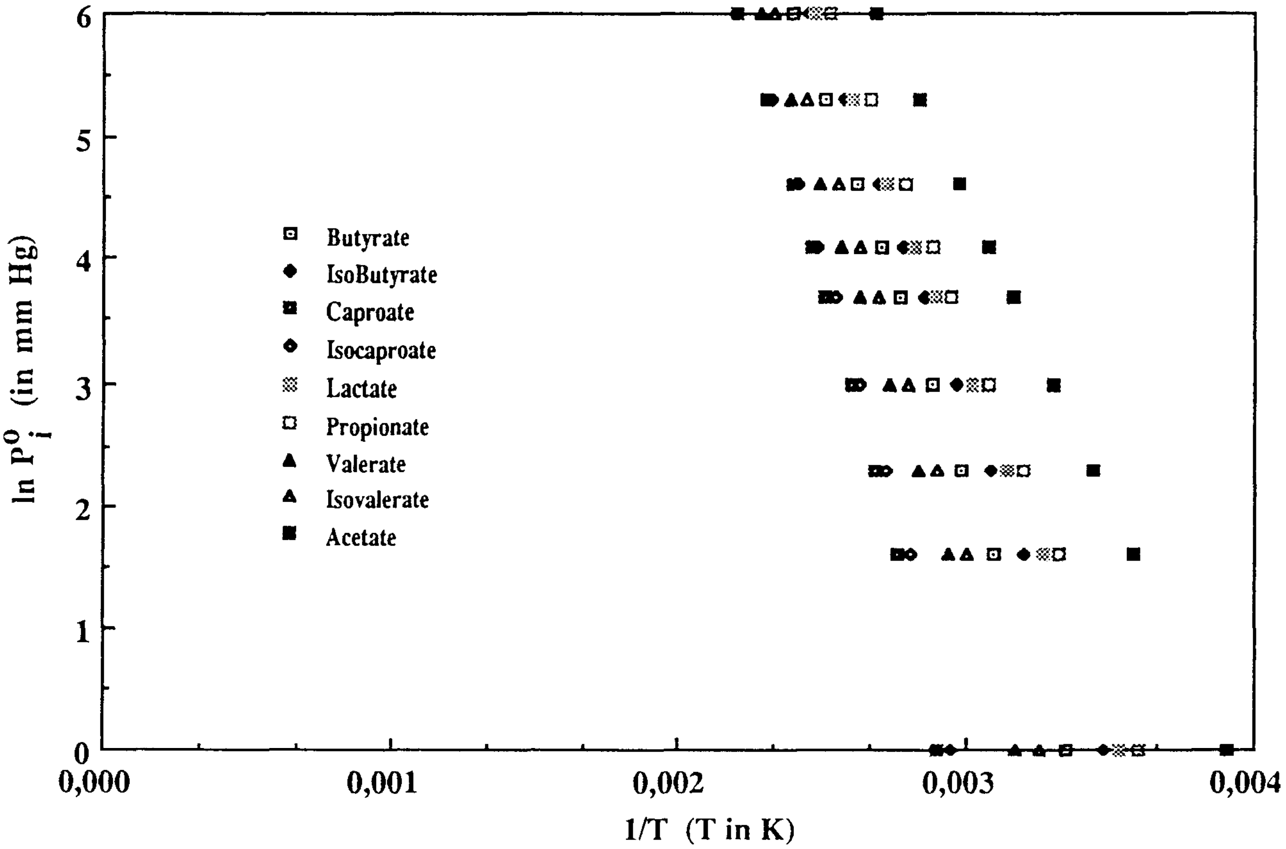


Figure 3: Vapor pressures of organic compounds as a function of temperature ; ln P^o_i=f(1/T)

The correlation adopted is an ANTOINE law expression of which coefficients (A, B, C) are identified from experimental data using a Gauss-Newton method in order to minimise the criterion ($\Sigma\,(X_{data}-X_{model})^2$). The obtained coefficients are reported in table 4.

Table 4: ANTOINE law coefficients of organic compounds.

Compound	A	B (K)	C (K)	Standard deviation	Temperature range (K)
Acetic acid	18.7013	4595.0	-10.3592	+/- 0.31%	255.95 - 391.25
Propionic acid	18.7247	4659.6	-28.9296	+/- 0.24%	279.75 - 414.25
Lactic acid	17.7051	4231.2	-43.7948	+/- 0.26%	282.75 - 424.65
butyric acid	19.3598	5129.3	-33.7980	+/- 0.25%	298.65 - 436.65
Isobutyric acid	19.7277	5410.6	-13.6817	+/- 0.31%	287.85 - 427.65
Valeric acid	20.6629	6215.7	-14.5356	+/- 0.19%	315.35 - 448.25
Isovaleric acid	19.9495	5602.8	-26.9055	+/- 0.34%	307.65 - 448.25
Caproic acid	14.1332	2127.9	-193.568	+/- 1.26%	344.55 - 475.15
Isocaproic acid	12.9469	1756.9	-202.905	+/- 2.09%	339.35 - 480.15

2.3 - Influence of pH

Several compounds in the liquid phase exist under different forms: dissociated and non dissociated. It is the case of carbon dioxide (CO_2) which exists under 3 forms in solution, CO_2, HCO_3^- (bicarbonate form), CO_3^{2-} (carbonate form). As shown in T.N. 17.1 the ratio of these 3 forms mainly depends on the pH value.

The dissociation of the compound AH in water can be represented by the following reaction:

$$AH + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^- + H_3O^+$$

The equilibrium constant K_a for the reaction is expressed by:

$$K_a = \frac{[A^-].[H_3O^+]}{[AH]}$$

It must be outlined that this expression of the equilibrium is generally considered as invariant near infinite dilution for all the species (except water). Such an assumption corresponds to an ideal behaviour for all the components of the solution. More sophisticated technics will be considered in the next section with the introduction of the activities of the different species.

Considering the definition of pH, $pH = -\log[H_3O^+]$ or $[H_3O^+] = 10^{-pH}$, the concentration of a dissolved form in solution can be calculated, as shown below, as a function of pH, of the non dissolved form and of the equilibrium constant K_a.

$$[A^-] = \frac{K_a\,[AH]}{10^{-pH}}$$

The equilibrium constant depends on physical and on chemical conditions of the solution. As it is supposed that there is no interaction between the chemical components, the equilibrium constant can be expressed only as a function of temperature: $K_a(T)$.

Thus we can write:

$$[A^-] = \frac{K_a(T)\,[AH]}{10^{-pH}} = \xi(T,pH)\,[AH]$$

Considering $[AH]^{tot}$, the sum of dissolved and non dissolved form of AH,

$$[AH]^{tot} = [A^-] + [AH]$$

$$[AH]^{tot} = [AH]\left(1 + \xi(T,pH)\right)$$

2.3.1 - pH and gas-liquid equilibrium

The gas-liquid equilibrium (the distribution of a compound between the liquid and the gas phases) can be determined from the partition coefficient k_i:

$$k_i = \frac{y_i}{x_i}$$

If the compound exists in dissociated and non dissociated forms, for a same value of the partition coefficient k_i, the total quantity of the compound (dissociated and non dissociated forms) changes with the pH. In order to determine the total fraction of a compound i (dissociated and non dissociated forms) in a liquid phase, a new expression of k_i must be proposed, taking into account the effect of pH. The new partition coefficient k_i^{ap} is a function of pH and temperature:

$$k_i^{ap} = \frac{y_i}{x_i^{tot}}$$

$$k_i^{ap}\,(T,pH) = \frac{\left(k_i(T) + y_i\,\xi(T,pH)\right)}{1 + \xi(T,pH)}$$

where

$$\xi(T,pH) = \frac{[\text{i dissociated}]}{[i]}$$

2.3.2 Determination of ξ(T,pH) for ammonia

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_{NH_3} = \frac{[OH^-]\,[NH_4^+]}{[NH_3]}$$

Considering $[OH^-].[H_3O^+] = 10^{-14}$, then

$$[NH_4^+] = \frac{K_{NH_3}(T)}{10^{pH-14}}\,[NH_3]$$

and

$$\xi(T,pH) = \frac{K_{NH_3}(T)}{10^{pH-14}}$$

A relation giving K_{NH3} as a function of temperature can be established from experimental data reported in table 5. The expression chosen to calculate $K_{NH3}(T)$ is the same as the one presented by Edwards and al. (8) for the dissociation constants of carbon dioxide in water:

$$\ln K_{NH_3}(T) = \frac{A_1}{T} + A_2 \ln T + A_3 T + A_4$$

The coefficients A_1, A_2, A_3, A_4 are identified by using a Gauss-Newton method (criterion = $\Sigma\,(X_{data}-X_{model})^2$).

It must be outlined that for the 4 coefficients calculated by Edwards (6) for CO_2, the third (A_3) is equal to 0; thus the relations giving the dissociation constant of CO_2 as a function of temperature appear as 3 parameters relations (1).

Table 5: dissociation constants of ammonia from 0 to 50°C

Temperature °C	0	5	10	15	20	25	30	35	40	45	50
Ammonia $K_{NH3}\ 10^5$	1.374	1.479	1.570	1.652	1.710	1.774	1.820	1.849	1.862	1.879	1.892

The following results are obtained, for the identification of the coefficients from the experimental data (9), with a criterion equal to 1.11 10^{-4}:

A_1= -26 134.2
A_2= -149.005
A_3=0.211
A_4= 862.706
Standard deviation = 0.15%
Temperature range: 273.15 - 333.15 K

For the same model, different parameters are proposed by Edwards (8), for a largest temperature range:

A_1= -3 335.7
A_2= 1.4971
A_3=-0.0370566
A_4= 2.76
Temperature range: 273.15 - 498.15 K

The differences between the two set of parameters show the sensibility of parameters values to the temperature range, indicating coupling between parameters.

2.3.3 - Determination of ξ(T,pH) for organic acids

The organic acids considered in this study are all mono acids (AH), thus a same dissociation equation can be used for all of them:

$$AH + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^- + H_3O^+$$

and then considering the previous relations

$$\xi(T,pH) = \frac{K_a(T)}{10^{-pH}}$$

The expression of $K_a(T)$ can be determined by the method used for $K_{NH3}(T)$. Except for acetic acid, propionic acid and butyric acid, the experimental data (table 6 and table 7) are too scarce to allow a reliable identification of the coefficients. When it is possible, the parameters of the following expression of $K_a(T)$ are identified (table 8),

$$\ln K_a(T) = \frac{A_1}{T} + A_2 \ln T + A_3 T + A_4$$

and in the other cases, $K_a(T)$ is supposed to be unaffected by the temperature and remains equal to the value reported in table 6.

Table 6: dissociation constants of acids in water at various temperatures (9)

Temperature	°C	0	5	10	15	20	25	30	35	40	45	50
Acetic acid	$K_a\ 10^5$	1.657	1.700	1.729	1.745	1.753	1.754	1.750	1.728	1.703	1.670	1.633
Propionic acid	$K_a\ 10^5$	1.274	1.305	1.326	1.336	1.338	1.336	1.326	1.310	1.280	1.257	1.229
butyric acid	$K_a\ 10^5$	1.563	1.574	1.576	1.569	1.542	1.515	1.484	1.439	1.395	1.347	1.302
lactic acid	$K_a\ 10^4$	1.287	-	-	-	-	1.374	-	-	-	-	1.270

Table 7: dissociation constants of organic acids in aqueous solutions (9)

	Temperature °C	K_a
Isobutyic acid	18	$1.44\ 10^{-5}$
Valeric acid	18	$1.51\ 10^{-5}$
Isovaleric acid	25	$1.7\ 10^{-5}$
Caproic acid	18	$1.43\ 10^{-5}$
Isocaproic acid	18	$1.46\ 10^{-5}$

Table 8: Identification of parameters (from table 6)

	A_1	A_2	A_3 (K^{-1})	A_4	Standard deviation
Acetic acid	-3887.2	-7.8519	-0.01795	52.1770	0.03%
Propionic acid	-12560.6	-65.978	0.0787	383.338	0.045%
Butyric acid	-1879.5	-109.049	0.15007	628.5	0.04%

Therefore, the gas-liquid equilibrium model has the following advantages:

1- by taking into account the dissociation of weak electrolytes, the overestimation of the partial pressure of compounds reacting in solution is limited, what is observed if the dissociation effect is neglected (Edwards et al.) (8);

2- the model, based upon the determination of one single correlation, is easy to introduced in the thermodynamical description of the flash module of the ProSim simulator (T.N. 17.1) (1).

Nevertheless, this model must be improved considering the non ideal solution behaviour of some solutes.

III - CHEMICAL AND GAS-LIQUID EQUILIBRIUM MODEL FOR WEAK ELECTROLYTES AT INFINITE DILUTION

3.1 - Thermodynamic description of gas-liquid equilibrium

3.1.1 - General description

In a multiphasic system, the thermodynamic equilibrium is reached when all compounds are at equilibrium conditions between each phase. This equilibrium can be described through the equality of the fugacity (f_i) of each compound in each phase.

Considering a gas-liquid equilibrium, the relation is then:

$$f_i^L = f_i^G$$

f_i^L: fugacity of compound i in solution
f_i^G: fugacity of compound i in the gas phase

The fugacity f_i^L can be expressed as follows:

$$f_i^L = a_i\, f_i^{oL}$$

where a_i is the activity in solution of the compound i and f_i^{oL} the fugacity at standard state (as a function of T and P); a_i is then defined as a ratio of fugacity:

$$a_i = \frac{f_i^L}{f_i^{oL}}$$

An activity a_i is then defined for only one standard state and represents the deviation between this standard state and the actual fugacity in the solution of the compound i. Usually, the activity is associated to the molar fraction scale through the relation

$$a_i = \gamma_i\, x_i$$

x_i molar fraction
γ_i activity coefficient in the molar scale

The fugacity f_i^G of a compound is usually expressed as:

$$f_i^G = \Phi_i\, P_i$$

where Φ_i is the fugacity coefficient and P_i the partial pressure of compound i.

If the activity is now defined in the pure liquid standard state, the gas-liquid thermodynamic equilibrium of a compound i can be expressed by:

$$f_i^G = a_i\, f_i^{oL} = \gamma_i\, x_i\, f_i^{oL}$$

thus

$$\Phi_i\, P_i = \gamma_i\, x_i\, f_i^{oL}$$

or

$$\Phi_i\, y_i\, P_t = \gamma_i\, x_i\, f_i^{oL}$$

Considering the definition of the partition coefficient k_i:

$$k_i = \frac{y_i}{x_i}$$

a new expression of k_i is then obtained from the previous relations:

$$k_i = \frac{\gamma_i\, f_i^{oL}}{\Phi_i\, P_t}$$

k_i depends on temperature, pressure and on interaction between the different compounds both in the liquid and in the gas phases. The calculation of k_i for all compound involved in the gas and in the liquid phases is sufficient to determine the total gas-liquid equilibrium at T and P.

It must be outlined that γ_i is the activity coefficient in the molar scale with a pure liquid standard state *i.e.* $\gamma_i = 1$ if $x_i = 1$. This activity coefficient at infinite dilution will be noted γ_i^∞ :

$$\lim_{x_i \longrightarrow 0} \gamma_i = \gamma_i^\infty$$

From the gas-liquid thermodynamic equilibrium relation, an expression of f_i^{oL} (T,P) can be determined for the 'pure compound' standard state:

1- if the compound exists as a pure liquid at P and T:

$$f_i^{oL} = \Phi_i\, P_i^o$$

Φ_i fugacity coefficient of pure compound i

P_i^o vapour pressure of i (depends only on temperature)

2- if the compound exists only as a gas at T and P, a Poynting term must be added:

$$f_i^{oL} = \Phi_i\, P_i^o\, e^{-\int_P^{P_i^o} \frac{v_i^L}{RT} dP}$$

3.1.2 - Simplified relations

-Standard state fugacity-

The Poynting term remains equal to 1, at ordinary conditions (P<10 bars, T<400 K); thus it is usually neglected. The fugacity coefficient of the pure compound , Φ_i, can be neglected too if the gas is supposed to have a perfect behaviour (Φ_i #1). A global relation for the determination of 'pure compound' standard state can be established:

$$f_i^{oL} = P_i^o$$

-Fugacity of i in the gas phase (f_i^G)-

As mentioned above, the fugacity coefficient Φ_i is usually neglected (Φ_i #1) as the gas is supposed to have a perfect behaviour. It is important to note that this assumption can not be made when compounds react in the gas phase (as associations for carboxylic acids) or for high temperature ($T/T_c>0.6$).

Considering this assumption:

$$f_i^G = P_i$$

-Equilibrium relation-

With these previous assumptions, the equilibrium relation becomes:

$$y_i P_t = \gamma_i x_i P_i^o$$

thus,

$$k_i = \gamma_i \frac{P_i^o}{P_t}$$

with the previous definition of γ_i

3.2 - Description of weak electrolytes dissociation in solution

Like the gas-liquid equilibrium, the description of weak electrolytes dissociations in water can be represented through thermodynamical relations.

3.2.1 - Thermodynamic description of the dissociation

The dissociation of electrolytes in water generates news species neutral or ionised (water itself is ionised to H^+ or H_3O^+ and OH^-). The thermodynamic properties of mixtures depend on the forces among the species in solution. Aqueous mixtures are characterised by 3 main kinds of interactions:

1- physical interactions which result mainly from the dispersion forces (enthalpic effect) between the molecules (10);

2- chemical interactions which arise through the chemical properties of particular group inside molecules (association and solvation phenomena when the distance between molecules is moderate);

3- electrostatic interactions due to the electric charges on ionic species (11).

A weak electrolyte (such as carboxylic acids) is dissociated in water into ionic forms and an equilibrium is set up between the different ionic and non ionic forms. The following reaction represents such an equilibrium for a weak electrolyte (CA) and its cationic (C) and anionic (A) forms:

$$C_{\nu_C}A_{\nu_A} \rightleftharpoons \nu_A A^{z_A^-} + \nu_C C^{z_C^+}$$

ν_A and ν_C : stoichiometric coefficients

z_A and z_C : absolute value of ionic charges

A thermodynamic constant can be determined to characterise the chemical equilibrium between the different species involved. This constant K_{CA} represents the activity ratio of the compounds present in the equilibrium. K_{CA} depends only on temperature and pressure.

$$K_{CA}(T,P) = \frac{a_C^{*\nu_C}\, a_A^{*\nu_A}}{a_{CA}^{*}} = \frac{\gamma_C^{*\nu_C}\, \gamma_A^{*\nu_A}}{\gamma_{CA}^{*}}\, \frac{x_C^{\nu_C}\, x_A^{\nu_A}}{x_{CA}}$$

$K_{CA}(T,P)$ represents a true equilibrium constant which does not change with the solution composition. The activities can be defined either in molar or in molal scale and with a pure or an infinite standard state. By convention and for practical reasons the activities of charged species and the activities of all solutes will be considered in a molar scale with an infinite dilution standard state.

These activities are noted a_i^*:

$$a_i^* = \gamma_i^* \, x_i$$

$$\lim_{x_i \to 0} \gamma_i^* = 1$$

Moreover, the conversion between infinite dilution and pure standard state is easily written:

$$\gamma_i^* = \frac{\gamma_i}{\gamma_i^\infty}$$

$$a_i^* = \frac{a_i}{\gamma_i^\infty}$$

In the case of water, the following relation is written:

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w(T,P) = \frac{a_{H^+}^{*}\, a_{OH^-}^{*}}{a_w}$$

and a_w is always the activity of water in the pure liquid standard state

For a weak electrolyte in water, the following system can be formulated to describe the solution, using the thermodynamic constants, the electroneutrality conditions and the mass balance equations:

$$K_{CA}(T,P) = \frac{a_C^{*\nu_C}\, a_A^{*\nu_A}}{a_{CA}^{*}}$$

$$K_w(T,P) = \frac{a_{H^+}^{*}\, a_{OH^-}^{*}}{a_w}$$

$$n_{H^+} + n_C z_C = n_{OH^-} + n_A z_A$$

$$n_{o,w} = n_w + n_{OH^-}$$

$$n_{o,CA} = n_{CA} + \frac{n_A}{\nu_a} = n_{CA} + \frac{n_C}{\nu_C}$$

Such a system can be extended to more than 2 compounds (CA and water). The concentration of each species in solution can be calculated by solving the previous system. This requires to know:

1- the initial quantity of weak electrolyte $n_{o,CA}$ and water $n_{o,w}$;
2- the dissociation reaction ;
3- the value of $K_{CA}(T,P)$ and $K_w(T,P)$;
4- the activities of the different species, *i.e.* the activity coefficient γ_i. In fact the knowledge of the activity coefficient allows, through thermodynamic relations, to access to all thermodynamic and energetic properties of the mixture.

3.2.2 - Determination of activity coefficients

The three kinds of interactions, taken into account to represent the thermodynamic properties of a mixture, can be aggregated in 2 terms: long range interactions (LR) as ionic interactions, and short range interactions (SR) as physical and chemical interactions. An activity coefficient can be determined for each of these two interactions (γ_i^{SR} and γ_i^{LR}), and the activity coefficient γ_i of a compound i in mixture is then:

$$\ln \gamma_i = \ln \gamma_i^{SR} + \ln \gamma_i^{LR}$$

A lot of specific models exists in the literature for each type of interaction. The purpose of this note is not to list all of these models which are described by Achard (1992) (12).

From his investigation , Achard has selected one specific model for each of type of interaction (LR and SR), which are added to obtain a model suitable to predict thermodynamic properties in ionic and non ionic solutions. The long range interactions are described using the Pitzer Debye Huckel (PDH) model (Pitzer, 1980) (13). The short range interactions are described using a UNIFAC LARSEN (UL) model (Larsen et al., 1987) (14), which is based upon a group contribution method. To complete the model, the solvation effect (S) is taken into account . This correction is necessary to represent the non ideality of ionic mixtures, because of the chemical association phenomena between water and ions, which leads to the formation of clusters (the structural parameters of ions and by the way the activity coefficients are different).

The final global model is called ULPDHS model. Good results are obtained by using the model in cases of ionic solution for the calculation of water activity or boiling and freezing temperatures, and in the case of water-alcohol-electrolyte mixtures for the representation of the salting-out effects.

The activity coefficient required to solve the previous chemical equilibrium can then be determined using the ULPDHS method. But it must be noted that the model requires the knowledge of:

- the decomposition of the molecules in functional groups
- the interaction coefficients between groups
- the structural parameters of each group
- the physical conditions (T,P) and the molar fractions of each compound.

3.2.3 - Thermodynamic dissociation constants (K)

The thermodynamic constants are not available in the literature. Values of dissociation constants in the literature (often defined as acidity , Ka, or basicity ,Kb, constants) correspond to concentration ratios and are determined experimentally near infinite dilution, where solutions are assumed to be ideal. They remain constant if the mixtures behave ideally and in practice for very dilute mixtures. In real systems, concentration ratios change with composition.

To perform accurate calculation of true electrolyte mixtures, equilibrium constants have to account for solution non ideality. Nevertheless, to improve calculation of concentration of compound, equilibrium constants must refer to concentration ratios (K (c)), corresponding to the true mixture composition.

A global relation between K(c) and the equilibrium constant in ideal mixture ($K^{id}(c)$), generally available in literature, must be established. Considering the thermodynamic constant K to an infinite dilution standard state for a solute CA,

$$K_{CA}(T,P) = \frac{\overset{*}{\gamma}_C^{\,v_C}\,\overset{*}{\gamma}_A^{\,v_A}}{\overset{*}{\gamma}_{CA}}\,\frac{x_C^{v_C}\,x_A^{v_A}}{x_{CA}} = \left(v_m^L\right)^{(v_C+v_A-1)}\frac{\overset{*}{\gamma}_C^{\,v_C}\,\overset{*}{\gamma}_A^{\,v_A}}{\overset{*}{\gamma}_{CA}}\,\frac{C_C^{v_C}\,C_A^{v_A}}{C_{CA}}$$

C_i: concentration

$v_m{}^L$: molar volume of the mixture

superscript * refers to an asymmetric convention for solute, *i.e.* $\gamma_i{}^* = \gamma_i/\gamma_i{}^\infty$

The concentration ratio corresponding to the pseudo constant denoted K(c), which has been considered in the previous section, is defined as:

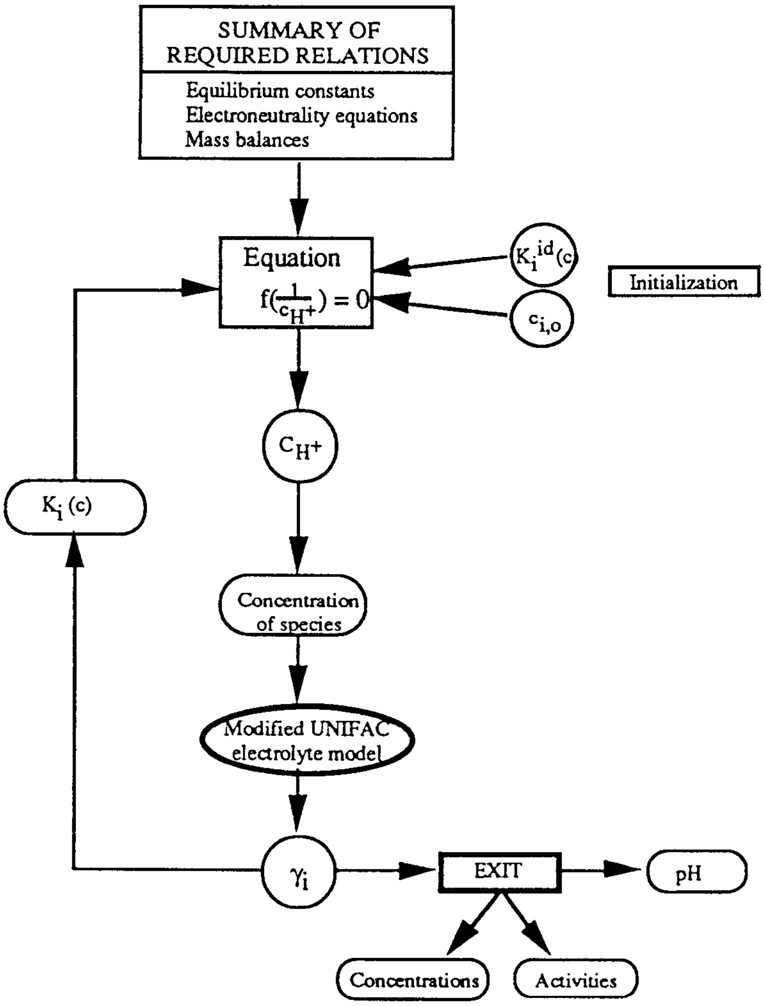
$$K_{CA}(c) = \frac{C_C^{v_C}\,C_A^{v_A}}{C_{CA}}$$

An expression linking K(c) and $K^{id}(c)$ can then be deduced:

$$K_{CA}(c) = \left(\frac{v_w^{oL}}{v_m^L}\right)^{(v_C+v_A-1)}\frac{\overset{*}{\gamma}_{CA}}{\overset{*}{\gamma}_C^{\,v_C}\,\overset{*}{\gamma}_A^{\,v_A}}\,K_{CA}^{id}(c)$$

Instead of K, K(c) is used to formulate the system representing a multicomponent mixture. The determination of the K(c) value can be made from the knowledge of the molar volume and activity coefficients in the mixture.

Such a system has been solved by Achard (15) in order to predict pH in aqueous mixtures using a ULPDHS model to calculate the γ_i and $\gamma_i{}^*$ values.



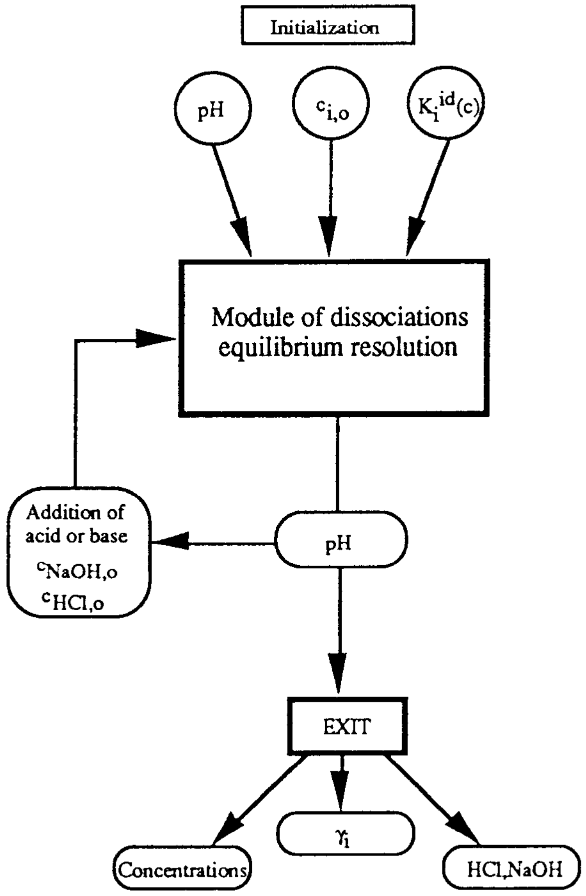


Figure 4: overall scheme for simultaneous calculation of concentrations, activity and pH

Figure 5: calculation of activity and concentrations at fixed pH conditions

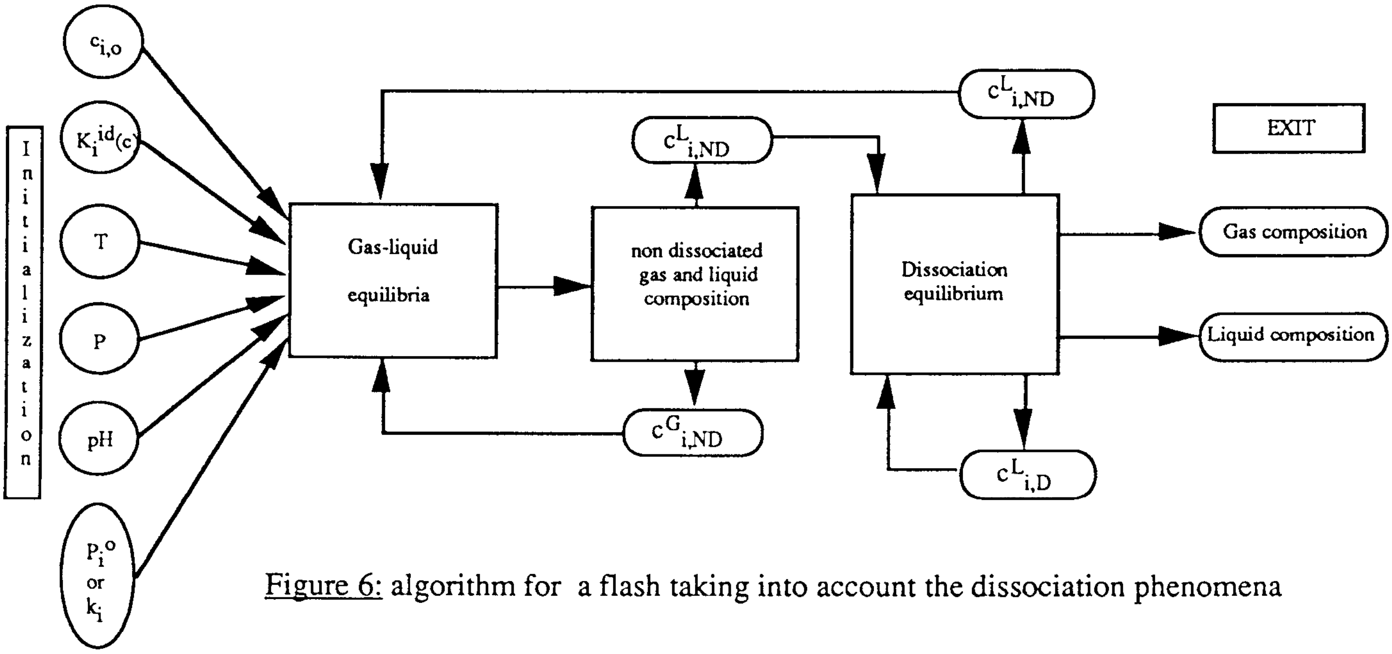


Figure 6: algorithm for a flash taking into account the dissociation phenomena

This method can be used to determine the concentrations of compounds in a fixed pH mixture and the added quantity of base (NaOH) or acid (HCl) to obtain this pH value. Figure 4 and 5 show respectively the algorithm developed to determine pH in true mixtures and the algorithm using the previous one as a module in order to obtain c_i and γ_i for a fixed pH mixture.

Thermodynamic relations are available to describe equilibrium in true mixtures and in perfect gas phase. These relations can be used and solved by a theoretical algorithm reported in figure 6, which allows to predict the composition both of the gas and of the liquid phase from the total quantity of non dissociated compound and from temperature, pressure and pH conditions.

Nevertheless, these calculations need to know values or relations giving the vapour pressure(P_i^o), the dissociation constants ($K^{id}(c)$), and parameters required for the ULPDHS model.

At the present time, all required coefficients to solve the system are not available. Moreover, in the present description of the MELiSSA loop dissociated compounds are not involved and a pH regulation through addition of NaOH or HCl is not considered. The system to be applied to the MELiSSA loop modelling must be simplified; thus instead of true mixture, the liquid streams involved in the MELiSSA loop are supposed to be infinite dilution solutions.

3.3 - Equilibrium relations at an infinite dilution

The previous relations established for gas-liquid and dissociation equilibrium can be simplified using an infinite dilution assumption for the solute in the liquid phase.

First it must be noted that for an infinite dilution solution, the activity coefficients remain constant whatever the composition of the solution for fixed temperature and pressure conditions. These activity coefficients are denoted γ_i^∞ and they could be calculated by using the UL model (LR interactions can be neglected). The γ_i^∞ values calculated for the compounds involved in the MELiSSA loop are reported in table 8.

Table 8: Activity coefficients of organic compounds at infinite dilution in water

Compound	Temperature °C	γ_i^∞
Acetic acid	25	1.4581
Butyric acid	25	2.3345
Isobutyric acid	18	2.0690
Propionic acid	25	1.7865
Valeric acid	18	2.7254
Isovaleric acid	25	3.1721
Caproic acid	18	3.6926
Isocaproic acid	18	2.7164
Lactic acid	25	1.0062

The gas-liquid equilibrium relation becomes

$$k_i = \gamma_i^{\infty} \frac{P_i^o}{P_t}$$

The dissociation constant $K_{CA}(c)$ becomes

$$K_{CA}(c) = K_{CA}^{id}(c)$$

These expressions are easy to link with the gas-liquid model presented in the first part of this note. By the same way k_i^{ap} can be calculated using the expression of k_i presented above:

$$k_i^{ap}(T,pH) = \frac{\left(k_i(T) + y_i\,\xi(T,pH)\right)}{1+\xi(T,pH)}$$

where ξ (T,pH) is defined from the constant dissociation $K_{CA}(c)$ as:

$$\xi(T,pH) = \frac{[\text{dissociated form of the compound}]}{[\text{non dissociated form of the compound}]}$$

The gas-liquid equilibrium model at infinite dilution presents the advantage of simplicity, like the gas-liquid equilibrium model for ideal solutions, but skips the main defaults of this previous model. The infinite dilution model, based upon well-defined thermodynamic relations, represents a more realistic system and minimises the interactions between compounds in solution what is necessary because of the difficulties to determine all these interaction.

Moreover, simulations of the MELiSSA loop can be performed in infinite dilution conditions, thus the results obtained from these simulations can be compared to a real behaviour of the loop.

CONCLUSION

Two models for the chemical and gas-liquid equilibrium have been developed. One is based upon the assumption of ideal behaviour of the system, and the other is based upon the assumption of an infinite dilution condition. They both present the advantage to be easy to introduced in the ProSim modules for the simulations, but the infinite dilution model is the most realistic.

In order to use the chemical and gas-liquid equilibrium model at infinite dilution conditions, the infinite dilution conditions are required. Actually it is difficult to know if the compounds presently involved are at infinite dilution in the loop. In fact, the volume of water (volume of liquids) in the compartments is not defined neither the wash water and the water for food preparation, and the control of the concentrations of the compounds in the compartments is not considered by the model the loop (1).

Thus, to perform simulations , a water management must be introduced in order to control the molar fraction of the compounds in all liquid streams of the loop by the control of the water molar fraction.

Nevertheless, the low attempted quantity of VFA and the important quantity of water involved in the loop lead to think that the infinite dilution behaviour is a realistic assumption.

To include new compounds in the loop (see table 2) needs to know, where and how they are produced and consumed or degraded, and then to be able to establish the stoichiometric equations for the production and the consumption of these compounds.

The building of these equations are under investigation and no simulations including these new compounds can be performed until this building was achieved.

At the present time, the pH is considered as a value and is not a result of a calculation ($pH = -\log [H_3O^+]$). When the major ionic species (acids, bases) will be introduced in the loop description, a pH regulation module could be introduced in the MELiSSA loop design in order to provide a pH regulation by the control of HCl and NaOH inputs.

The model determines the partitions of compounds in gas and liquid phases (*i.e.* the concentrations if the liquid volume is know). At the present time, assuming that there is no transfer and kinetics limitations, the model is sufficient to determine the gas and the liquid phases compositions. For the future, the model will be a tool to determine the values of C_i^*, one of the 4 parameters to know in order to model the compartments bio-processes. A special attention will be provide to compounds offering pH dependant chemical equilibria. All chemical forms are considered for a compound in the previous model, but only the gas dissolved form is considered in the gas-liquid equilibrium (C^*_i).

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