Estimation of equilibrium properties in formulation or processing of liquid foods

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Abstract

Water is the main component in most foods and equilibrium properties of water are considered as reference properties in food processing. Water activity is an example. This work is based on the UNIFAC method [*AIChE Journal* 21 (1975) 1086], which estimates equilibrium properties from the excess Gibbs energy of all compounds within the solution. It relies on the idea of group contribution in which each molecule is considered as a collection of basic building blocks, the functional groups. The advantage of the group contribution approach is that, from a relatively small number of groups, the properties of many different molecules can be obtained. This gives vapour–liquid properties, liquid–liquid or solid–liquid properties, osmotic properties, and by using dissociation constants values, this affords pH values. The UNIFAC model was modified. The relationship of Larsen et al. [*Ind. Eng. Chem. Res.* 26 (1987) 2274] accounts for short-range interactions; a Pitzer term based on the Debye-Hückel theory accounts for long-range interactions. Finally, hydration of ions or non-dissociated molecules is considered via a hydration number. This number characterises a specific ion, not a given salt, which facilitates the treatment of mixtures containing many dissociated or partly dissociated compounds. The model was used to estimate equilibrium properties (a_w, activity coefficient of salts and sugars) needed for modelling osmotic dehydration of foods, in production of flavouring agents by fermentation processes (pH, activity coefficient) and in food (e.g. cow's milk) formulation and control.
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Keywords: a_w; pH; UNIFAC; Pitzer; Solvation; Foods; Milk

1. Introduction

A major concern of food engineers is the design of equipment and processes for efficient transformation of large quantities of raw materials into finished products. In the design and operation of such processes, a large amount of reliable data on the equilibrium properties of materials is necessary. However, the limited availability of experimental data can hardly satisfy such an enormous demand. Engineers are then required to rely on a variety of methods for estimating physical properties of compounds of industrial interest. Food scientists have exactly the same problems when formulating foods.

This work concerned the use of a method, which, in addition to the equilibrium properties of water, affords equilibrium properties of all the components in aqueous solutions, such as liquid food solutions. Emphasis was placed on the modelling of properties of mixtures and particularly of activity coefficients in multicomponent mixtures with or without electrolytes. Activity coefficients give access to properties such as water activity, osmotic pressure, freezing point depression, boiling temperature increase, pH and acidity.

Our purpose was to compare predictions of the model with experimental results or situations encountered in food processing operations and in the specific case of milk quality control.

2. Thermodynamic model

Activity coefficient models first appeared in the pioneering work of Margules in 1890 and Van Laar in 1910. This was recently recalled in a very full review of past accomplishments in applied thermodynamics for process modelling by Chen and Mathias (2002). Van Laar and Margules identified the idea of liquid-phase non-ideality, and its representation by algebraic functions that have the correct limiting behaviour. Wilson (1964) contributed the all-important "local composition" concept that enabled correlation of non-ideal systems with only binary parameters. Prausnitz and his co-workers

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subsequently developed the NRTL (Renon & Prausnitz, 1968) and UNIQUAC (Abrams & Prausnitz, 1975) models, which are widely used in the industry today, especially for highly non-ideal systems.

Predictive (rather than correlative) activity coefficient methods were initially based on the regular solution theory of Scatchard and Hildebrand in 1929, but are now mostly based on group contribution models: ASOG (Wilson & Deal, 1962) and UNIFAC (Fredenslund, Jones, & Prausnitz, 1975). These methods have been well received, and there has been continued development of the UNIFAC binary interaction matrix (Gmehling, 1998) improving the range and accuracy of the method. New methods such as the COSMOS-RS (Eckert & Klamt, 2002; Klamt, 1995), Group Contribution Solvation model (Lin & Sandler, 1999), and Segment Contribution Solvation models (Lin & Sandler, 2002), which use techniques of quantum chemistry and molecular modelling, are being developed and improved.

Models for electrolyte activity coefficients are largely variations of the 1923 Debye-Hückel equation for the long-range ion–ion interaction contribution. Examples are the virial expansion extensions of Bromley in 1972 and Pitzer (1973). Recognising two critical characteristics of electrolyte solutions (local electro-neutrality and like-ion repulsion), Chen, Britt, Boston, and Evans (1982) extended the NRTL local composition model to electrolyte solutions. This model for aqueous electrolytes has been extended to zwitterions and organic electrolytes that form micelles when the electrolyte concentration exceeds the critical micelle concentration (Chen, Bokis, & Mathias, 2001).

Central to the thermodynamic modelling of electrolyte systems is an understanding of the speciation, i.e. the solution chemistry of electrolytes to form ions and complexes and to precipitate as salts (Chen, Mathias, & Orbey, 1999; Rafal et al., 1994). Robinson and Stokes (1959), then Achard, Dussap, and Gros (1994), clearly identified the need to define the ionic entity in terms of its degree of hydration.

For polymer systems, the classical Flory-Huggins lattice model of 1942 captures two key polymer characteristics: the size effect on the entropy of mixing and the interaction effect on the enthalpy term. Hard-sphere-chain models, such as SAFT (Huang & Radosz, 1990) and PHSC (Song, Lambert, & Prausnitz, 1994), which are based on theoretical statistical mechanics, yield successful engineering equations of state for polymer solutions. Recent polymer model developments attempt to account for additional polymer characteristics such as copolymer composition and polydispersity. Examples include the segment-based polymer NRTL (Chen, 1993) that integrates the segment concept with local composition models and the PHSC equation of state (Song et al., 1994) with segment-based mixing rules for copolymers.

Progress is being made in the modelling of chemical systems with multifunctional group molecules such as non-ionic and ionic surfactants. Extensions based on the polymer NRTL and UNIFAC models have been successful, and work on more complex molecules, such as proteins, is being pursued (Chen, King, & Wang, 1995; Curtis, Blanch, & Prausnitz, 2001).

Finally, in the food industry, we acknowledge the pioneering work of Le Maguer (1992), Achard, Dussap, and Gros (1992) and Catté, Dussap, and Gros (1994, 1995) on aqueous carbohydrate systems. Le Maguer used a UNIQUAC equation for the description of excess properties of aqueous carbohydrate systems. Achard et al. used the UNIFAC model of Larsen et al. to predict water activity related properties. Catté et al. introduced a physical chemical model that takes conformational equilibrium into account. It can thus distinguish among different isomers and anomers. Peres and Macedo (1997) and then Spiliotis and Tassios (2000) introduced new main groups to describe non-aqueous sugar solutions and mixed solvent mixtures such as ethanol/water or *n*-hexane/water.

3. Model formulation

3.1. General

Given the thousands of biochemical compounds of interest in food or biological processes and the lack of thermodynamic data for many of them, it was decided to focus on predictive group-contribution methods.

The thermodynamic properties of a mixture depend on the forces that exist between the species in the mixture. When electrolytes are considered, the system is characterised by the presence of both molecular species and ionic species, resulting in three different types of interactions: ion–ion, molecule–molecule and ion–molecule. Ion–ion interactions are governed by electrostatic forces between ions that have a much longer range than other intermolecular forces. Molecule–molecule and ion–molecule interaction forces are known to be short-range in nature. The excess Gibbs energy of systems containing electrolytes can be considered as the sum of two terms, one related to long-range forces between ions and the other to short-range forces between all the species. In this study different models for the excess Gibbs energy were tested extensively. We chose the Pitzer–Debye–Hückel expression (Pitzer, 1973, 1991) to represent long-range interactions while the local composition concept was used to represent the contribution of short-range interactions of all kinds.

3.2. Non-electrolyte mixtures

Among the various approaches used to develop local composition models for non-electrolyte systems, the

UNIFAC model as modified by Larsen, Rasmussen, and Fredenslund (1987) was selected.

$$\frac{g^E}{RT} = \frac{g^E}{RT}(PDH) + \frac{g^E}{RT}(UL) \tag{1}$$

Similarly

$$Ln\gamma_i = Ln\gamma_i^{PDH} + Ln\gamma_i^{UL} \tag{2}$$

As in the UNIQUAC (Abrams & Prausnitz, 1975) and in the well-known UNIFAC (Fredenslund et al., 1975) models, the excess Gibbs function was calculated as the sum of a combinatorial and a residual contribution:

$$\frac{g^E}{RT}(UL) = \frac{g_c^E}{RT} + \frac{g_r^E}{RT} \tag{3}$$

Two changes were introduced by Larsen et al. (1987):

1. The combinatorial term was restricted to the Flory-Huggins combinatorial with modified volume fractions following Kikic, Alessi, Rasmussen, and Fredenslund (1980).
2. The group-interaction parameters have been made temperature-dependent. The volume parameter and the surface area parameter for groups are the same as in UNIQUAC.

In liquid foods, carbohydrates are very common components. Examples of group decomposition are given in Table 1 for some common carbohydrates. The UNIFAC–Larsen model was used to predict the activity coefficients in aqueous solutions containing oligosaccharides or polyols, and calculate the activity of water and related properties such as the boiling point temperature and the freezing point depression. The average percentage error was defined as

$$APE = \frac{100}{N}\sum_{i-1}^{N}\left|\frac{V_{exp} - V_{calc}}{V_{exp}}\right| \tag{4}$$

where N is the total number of data points and "V_{exp}" and "V_{calc}" refer, respectively, to experimental and calculated equilibrium properties. APE ranges from 1% for a_w prediction to 0.05% for the boiling point temperature

and the freezing point temperature for binary mixtures containing monosaccharides (glucose, fructose, mannose, galactose, etc.), oligosaccharides (lactose, maltose, ...), polyols (glycerol, mannitol, propylene glycol, etc.) and multicomponent mixtures containing a small number of saccharides in water (Achard et al., 1992).

3.3. Electrolyte mixtures

In the case of strong electrolytes, the term of Pitzer based on the Debye–Hückel theory was added to the UNIFAC–Larsen model. Ions are considered as UNIFAC independent groups. The crystal ionic radii of the elements necessary to calculate the group volume and surface area parameters were these of Weast (1972). It was decided to take into account the solvation of charged species giving clusters by means of a hydration number for each ion at infinite dilution. A mixture containing water, one anion and one cation was then described using six group interaction parameters and two hydration numbers; this number was reduced, based on the following three assumptions:

1. Repulsive forces between ions of like charge are extremely large.
2. Interactions between ions of opposite charge are dominated by electrostatic forces and are accounted for by the PDH term.
3. The energy of interaction between two molecules of water can be obtained from the difference of internal energy between the gaseous and liquid states.

With this approach two interaction parameters (water-anion and water-cation interactions) were sufficient to characterise a water–salt system. These interaction parameters and the hydration number for each ion (Table 2) were evaluated for 43 anions and cations from a database of 110 water–salt systems. This model satisfactorily predicts water activity, osmotic coefficients and salting-out effects in aqueous mixtures of two or three electrolytes within less than 5% even for saturated solutions (Achard et al., 1994); it can be used for multielectrolyte solutions without adding any new interaction coefficient.

Table 1
Examples of decomposition of sugars into structural UNIFAC groups

Molecules		Number of structural groups				
		Alkanes CH$_2$	Alkanes CH	Alkanes C	Alcohols OH	Ethers CH–O–
Sucrose	C$_{12}$H$_{22}$O$_{11}$	3	5	1	8	3
Maltose	C$_{12}$H$_{22}$O$_{11}$	2	7	0	8	3
Glucose	C$_6$H$_{12}$O$_6$	1	4	0	5	1
Fructose	C$_6$H$_{12}$O$_6$	2	2	1	5	1
Glycerol	C$_3$H$_8$O$_3$	2	1	0	3	0
Mannitol	C$_6$H$_{14}$O$_6$	2	4	0	6	0

Table 2
Examples of hydration numbers Nh for ions used in this work

Component	Hydration number Nh
H$^+$	2.96
K$^+$	2.96
Na$^+$	2.61
Ca^{2+}	3.08
Mg^{2+}	3.93
NO$_3^-$	0.48

Other hydration numbers for anions are set at zero.

For systems of weak electrolytes (amino-acids, carboxylic acids, phosphates, carbonates, etc.) neither the concentrations of species in solution nor their activity coefficients are known. First, a special automatic procedure was used to generate the whole species in the mixture; for example, when Na_2HPO_4 is dissolved in water, the species Na^+, H^+, OH^-, HPO_4^{2-}, PO_4^{3-}, $H_2PO_4^-$, H_3PO_4 may be present in solution and should be considered. Secondly, the system constituted by dissociation constants of acids and bases at infinite dilution, the dissociation constant of water, the electroneutrality equation and stoichiometric balances was solved, giving the concentrations of all species in the mixture. This numerical procedure was coupled with the computing of activity coefficients, using the UNIFAC–Larsen–Pitzer–Debye–Hückel with solvation (ULPDHS) model, in order to calculate the dissociation constants in the actual non-ideal mixture, giving direct access to the pH of the solution, defined as:

$$pH = -\log_{10}(a_{H+}) \tag{5}$$

Figs. 1 and 2 compare the results given by the model for two amino acids, aspartic acid, with changed polar side chains and glycine, with non-polar side chains, with experimental values (Fasman, 1992; Weast, 1972). This clearly shows the possibilities of the method in a completely predictive situation. It must be stressed that pH is represented satisfactorily if considered as the activity of H^+. No experimental value corresponding to the single ion H^+ has been used when fitting UNIFAC group interaction parameters. This confirms that the ULPDHS model correctly predicts the activities of ionic species.

4. Examples: processing of liquid foods and food formulation and control

4.1. Processing of foods

In the osmotic dehydration processes, foods are immersed in aqueous concentrated solutions containing salts, sugars or both. Dehydration of meat is achieved in sugar and salt solutions and the residence time depends on water activity differences between the solution and the meat, and on the relative values of diffusion coefficients of water, salts and sugars in meat. There are many ways to lower the activity of water but they are not equivalent for the quality of the processed meat and the model was used to design the solution in such a way as to obtain dried meat by removing water while controlling salt uptake. Some solutions defined to obtain an activity of water of 0.85 were tested in a meat dehydration process, and a solution containing 1 kg water, 200 g NaCl, 420 g sucrose and 1 g xanthan gum was finally adopted (Emam Djomeh, Djelveh, & Gros, 2001).
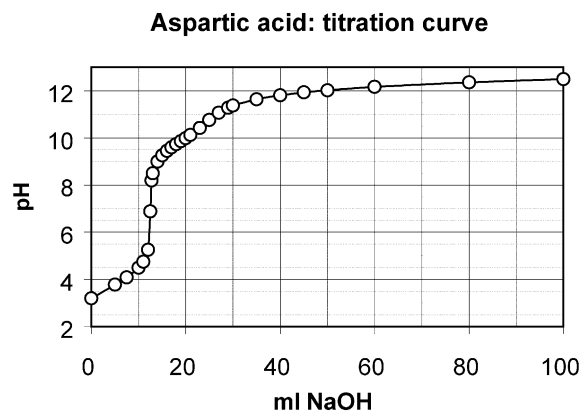
Aspartic acid: titration curve

Fig. 1. Titration curve of aspartic acid: 50 ml of 0.025 M solution of aspartic acid. *x* ml of 0.1M NaOH diluted to a total of 200 ml. Solid line: calculated values from the model, circles: data from Weast (1972).
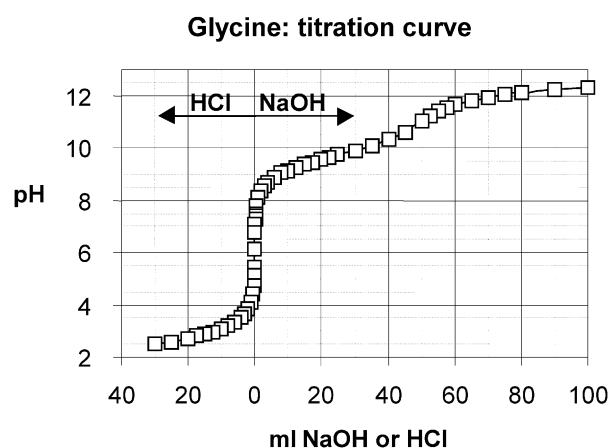
Glycine: titration curve

Fig. 2. Titration curve of glycine: 50 ml of 0.1 M solution of glycine and *x* ml of 0.1 M solution of sodium hydroxide or hydrochloric acid, diluted to a total of 200 ml. Solid line: calculated values from the model, squares: data from Fasman (1992).

Acetic acid is the major characterising component of vinegar. Vinegar functions in pH reduction, control of microbial growth and enhancement of flavour. It has found use in a variety of products, including condiments, such as ketchup, mustard, mayonnaise and relish, salad dressings, marinades, canned fruits and vegetables. Fermentation, conducted under controlled conditions, is the commercial method for vinegar production (Frings process).

Bacterial strains of *Acetobacter* and *Acetomonas* produce acetic acid from alcohol which has been obtained from a previous fermentation involving a variety of substrates, such as grain and grapes. During acetic production, large quantities of acetic acid and alcohol are released outdoors in the gas phase and are considered as air pollutants (VOCs, volatile organic compounds). Fig. 3 gives the partial pressure of acetic acid over an acetic acid solution calculated as

$$P_{AA} = \gamma_{AA} P_{AA}^0 x_{AA} \tag{6}$$
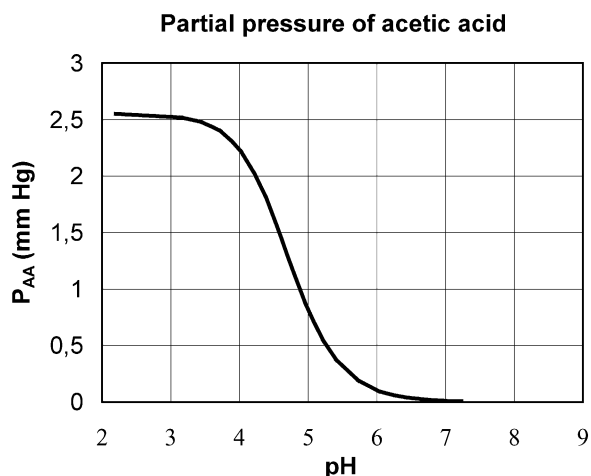
Partial pressure of acetic acid

Fig. 3. Partial pressure of acetic acid at 20 °C in an acetic acid–NaOH–water system as a function of pH.

as a function of pH. γ_{AA} is the activity coefficient of acetic acid (protonated form) in the solution, x_{AA} its mole fraction and P_{AA}^0 the vapour pressure.

Table 3 presents the values of the activity coefficient for the main components encountered at a given time during vinegar production. These values give direct access to VOCs emissions into the atmosphere and have helped to define a fed-batch culture policy, reducing VOC emissions by 30% (Bohatier, 1999).

Citric acid is the most widely used organic acid in the food industry, accounting for more than 60% of all acidulants consumed. It is commonly added to non-alcoholic beverages where it complements fruit flavour, contributes tartness, acts as a preservative and controls pH so that the desired sweetness characteristics can be achieved. Sodium citrate subdues the sharp acid note in highly acidified carbonated beverages; in club soda it imparts a cool saline taste. In hard confectionery, buffered citric acid imparts a pleasant tart taste; it is added to the molten mass after cooking as this prevents sucrose inversion and browning. Fig. 4 shows the behaviour of a citrate buffer resulting from a mixture of sodium citrate solution and citric acid solution (Fasman, 1992). The

Table 3
A typical composition of the fermentation medium during the production of vinegar from alcohol (Bohatier, 1999)

Component	Concentration (g l^{-1})	γ_{water}^{∞}	γ_{medium}
Water	to 1.000 l	1.0	1.0
Ethanol	16.0	5.4	4.1
Acetic acid	120.0	3.8	3.0
Frings salts	1.7		
Frings glucose	1.0	0.88	0.66
Ethyl acetate	0.05–0.3	71	39
Acetaldehyde	0–0.2	2.7	2.2

Molar activity coefficients for vinegar components in the fermentation medium, compared to values in water at infinite dilution γ_{water}^{∞}. pH = 2.15; a_w = 0.958.
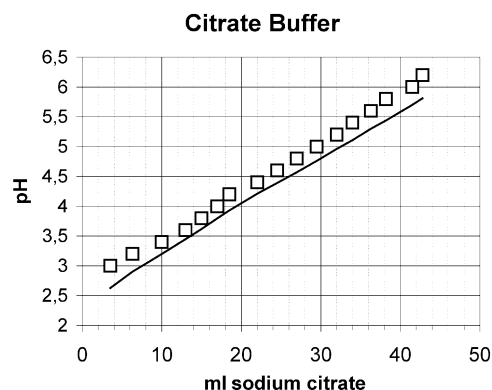
Citrate Buffer

Fig. 4. Citrate buffer: 0.1 M solution of citric acid; 0.1 M solution of sodium citrate. x ml of citric acid solution and $(50-x)$ ml of sodium citrate solution diluted to a total of 100 ml. Solid line: calculated values from the model, squares: data from Fasman (1992).

model underestimates the pH values and the differences between calculated and experimental values range between 0.05 and 0.4 pH units. This is not the case for the citrate phosphate buffer (Fig. 5) where the differences are lower then 0.1 pH unit except at pH = 7 (0.15 pH unit).

Sparkling ciders and other drinks are generally prepared by artificial carbonation to a level of 2.5–4.5 bars. Fig. 6 gives the calculated values and the experimental values (Fasman, 1992) of the carbonate-bicarbonate buffer in a pH range where experimental values are easier to obtain because dissolved CO_2 concentration is negligible; pH is underestimated with a maximum difference of 0.2 pH unit (at pH = 10).

Prediction of pH in commercial liquid foods is thus possible if the exact composition is known. The pH value of a high energy drink is reported in Table 4 and compared with the experimental values; the difference can be attributed to the approximate values given on the packaging by suppliers.
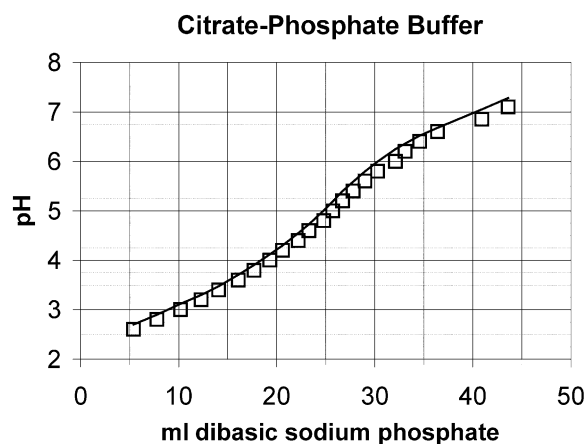
Citrate-Phosphate Buffer

Fig. 5. Citrate-phosphate buffer: 0.1 M solution of citric acid; 0.2 M solution of dibasic sodium phosphate. x ml of citric acid solution and $(50-x)$ ml of phosphate solution diluted to a total of 100 ml. Solid line: calculated values from the model, squares: data from Fasman (1992).
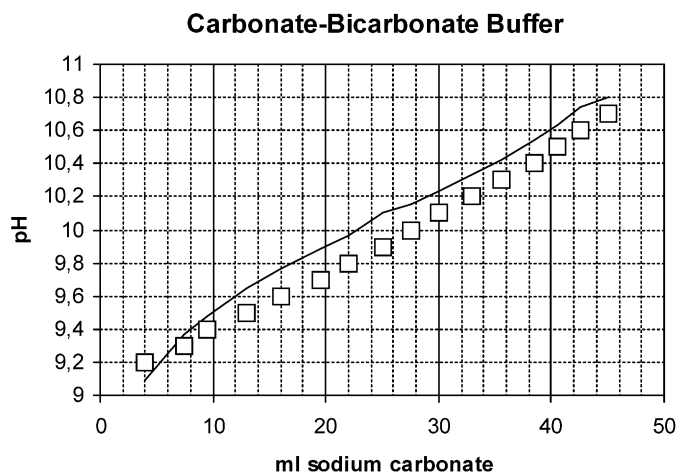
Carbonate-Bicarbonate Buffer

Fig. 6. Carbonate-bicarbonate buffer: 0.2 m solution of anhydrous sodium carbonate. 0.2 M solution of sodium bicarbonate. x ml of sodium carbonate solution and (50-x) ml of sodium bicarbonate solution diluted to a total of 200 ml. Solid line: calculated values from the model, squares: data from Fasman (1992).

Table 4
Calculated and experimental properties of a high-energy drink

Components	Concentration (mmol l^{-1})	
Total sugars (glucose, sucrose, fructose)	232	$pH_{calc} = 8.20$
NaCl	12	$pH_{exp} = 8.30$
Magnesium lactate	0.62	$a_w = 0.995$
Calcium bicarbonate	2.00	
Potassium gluconate	0.85	

4.2. Formulation of a model milk—quality control

The ULPDHS model was used as a tool to help define a model milk. Milk is a complex biological fluid, consisting of proteins, fat, lactose, minerals and vitamins in water (Table 5). Most of the water is free but a small amount hydrates the lactose and salts and some is bound to the proteins.

The proteins may be divided into two categories, the caseins and the soluble proteins, which included enzymes. The caseins form about 80% (w/w) of the total proteins and are almost entirely organised into micelles. The soluble proteins, called "whey proteins" because they separate into the whey during cheese making, consist of β-lactoglobulin, α-lactalbumins, immunoglobulins and serum albumin in decreasing amounts.

The lipids in milk are in the form of globules; there are 15 major fatty acids with chain length from $C_{4:0}$ to $C_{18:3}$. The diet of the animal has considerable influence on the fatty acid profile. Nevertheless palmitic and oleic acids represent about 50% (w/w) of total fatty acids. They are not soluble in water; conversely butyric (C_4) and caproic (C_6) acids are soluble in water.

Milk contains many salts (Buttriss, 1993). The potassium, sodium and chloride concentrations (with lactose) ensure that it is iso-osmotic with the blood. Colloidal calcium, magnesium, inorganic phosphate and citrate

Table 5
The composition of bovine milk. Typical concentration of the major components (adapted from Mathieu, 1998)

Component	Concentration (g l^{-1})	
Water	902	
Lactose	49	
Proteins	32	
Caseins		26
Whey proteins		6
Lipids	38	
Saturated fatty acids		
• soluble in water		1.9–3.4
• insoluble in water		19
Unsaturated fatty acids		
• mono-unsaturated		10.2
• polyunsaturated		0.9
Salts	9	1.23
Calcium		0.5
Sodium		1.51
Potassium		0.13
Chloride		1.11
Citrate		1.70
Phosphate		1.93
Bicarbonate		0.15

are associated with the casein content of the milk. The concentration of diffusible calcium and magnesium are closely related to soluble citrate concentration; the concentration of Ca^{2+} is inversely proportional to HPO_4^{2-} and highly pH-dependant.

Some other physiochemical characteristics of cow's milk include (Hurley, 2002):

- pH of normal milk is about 6.6–6.9
- osmotic pressure is about 700 kPa
- freezing point depression is about 0.54 K
- ionic strength is about 0.08 molar
- water activity is about 0.993.

Caseins form large micelles and lipids form still larger fat globules, due to their very low solubility in water. To create a milk model with the above physicochemical properties, we made the following three assumptions:

1. The physicochemical properties of milk are controlled by properties in the water phase (plasma phase of milk or skim milk).
2. The small quantity of lipids soluble in water is assimilated to butyric acid.
3. The protein behaviour is highly simplified by considering only caseins as representatives of casein in milk. An average casein protein was defined from the percentage and composition of α, β, κ and γ caseins (Mathieu, 1998). This made it possible to determine "average" basic or acid residues contained in caseins (Lys, Arg, Hist, Asp, Glu, Tyr and phosphoseryl residues) as stated in Table 6. Anions and cations interact with these residues.

Table 7 summarises the composition of two model milks, the difference between which is mainly the butyric acid content and the citrate salts composition.

Table 8 compares the calculated characteristic properties of these two milks with the properties of normal milk. The pH values remain within the range of normal milk. The water activity is equal to 0.994 for both the model milks.

Measurement of freezing point is used as a means of determining contamination of milk by water, either accidentally during milking and processing or fraudulently. It is usually in the range −0.53 °C to −0.57 °C with a mean of −0.54 °C. In general, 1% additional water in milk raises the freezing point by about 0.0055 °C. Freezing depression can be estimated from

Table 6
Characteristic data for caseins in cow milk (adapted from Mathieu, 1998)

Total caseins (g l^{-1})	26
α_{S1}	9.6
α_{S2}	2.9
β	8.9
κ	3.1
γ	1.0
Average molecular mass (g mol^{-1})	24,000
Averaged base or acid residues (per mole of average casein)	
Lysine	13
Arginine	5
Histidine	5
Aspartic acid	5
Glutamic acid	19
Tyrosine	8
Phosphoserine	6

Table 7
Tentative composition of model milks

Component	Model milk 1		Model milk 2
	Concentration		Concentration
	(g l^{-1})	(mol l^{-1})	(mol l^{-1})
Water	902	50.11	50.11
Lactose	49	0.143	0.143
Proteins (Caseins residues)			
Lys residue		0.0140	0.0140
Arg residue		0.0054	0.0054
Tyr residue		0.0086	0.0086
Phosphoseryl residue		0.0065	0.0085
Lipids			
Free fatty acids (butyric acid)	1.52	0.0173	0.0198
Salts			
NaCl	1.07	0.018	0.0175
KCl	0.85	0.0114	0.0114
K$_2$HPO$_4$	2.10	0.0121	0.011
MgHPO$_4$	0.18	0.0015	0.0014
CaHPO$_4$	1.10	0.008	0.008
Ca$_3$Cit$_2$	2.6	0.0052	0.0026
Mg$_3$Cit$_2$			0.0012
K$_3$Cit			0.0013
NaHCO$_3$	0.21	0.0025	0.0025

the value of the water activity in milk from the following general equation:

$$\ln a_w = \frac{\Delta H}{R}\left[\frac{1}{T_w} - \frac{1}{T}\right] - \frac{\Delta C_p}{R}\left[\ln\frac{T_w}{T} + \left(1 - \frac{T_w}{T}\right)\right] \quad (7)$$

where $\Delta H = 6008$ J mol^{-1} is the enthalpy of fusion of water at freezing point T_w, ΔC_p is the difference in the heat capacities of liquid water and ice ($\Delta C_p = 38.03$ J mol^{-1} K^{-1}) and T is the freezing point temperature of the mixture. The freezing temperature calculated is slightly lower than the experimental one, but we find, also, that the increase in freezing temperature due to addition of 1% water, is 0.0055 °C.

Titratable acidity is an estimate of the total acid in a solution. This is usually measured in milk at the start of

Table 8
Physical chemical characteristics of cow's milk (Hurley, 2002) and model milks

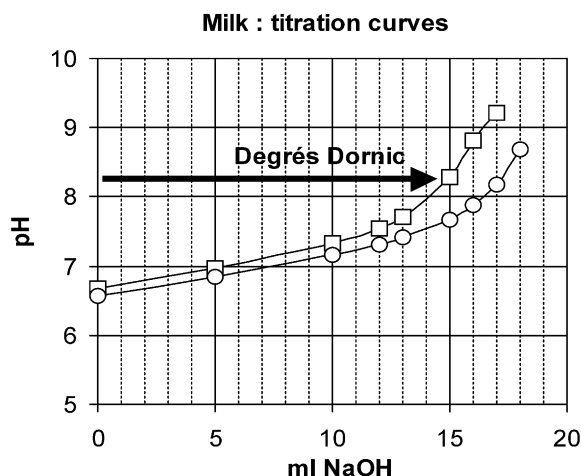|	Normal cow milk	Model milk 1	Model milk 2
pH	6.6–6.8	6.67	6.57
Osmotic pressure (kPa)	700	750	750
Freezing point depression (K)	0.53–0.57 (mean 0.54)	0.61	0.61
Ionic strengh (molar)	0.08		
Water activity	0.993	0.994	0.994
Acidity (°Dornic)	16–18	15	17

Milk : titration curves

Fig. 7. Titration curves of two milks with different butyric acid contents. 100 ml milk and x ml of 0.1111 M solution of sodium hydroxide. Acidity of milk is given in France in degrés Dornic; it is the value of x for which pH equals 8.3. Squares: model milk 1; circles: model milk 2.

cheesemaking as the baseline for the development of acidity by the starter bacteria which produce lactic acid. Phenolphthalein indicator is added to a measured quantity of milk diluted to twice its volume with carbon dioxide-free water. This is then titrated with 0.1111 M sodium hydroxide to a persistent pink colour (1 ml NaOH equivalent to 0.0010 g lactic acid). The result is expressed, in France, as degrés Dornic and the acidity of a normal milk must be in the range 16–19° Dornic (Mathieu, 1998). This is the case for the second model milk; the first one will be considered as "not rich, with low acidity and with a small buffering capacity" (Fig. 7 and Tables 7 and 8).

5. Conclusion

Although the accuracy of the results is still insufficient in some cases, we can anticipate that the modelling techniques that have been successful for the process industries will be extended to biological fluids and solids. Thermodynamic models will help to structure experimental knowledge and expertise, and to design new processes and extrapolate. They will help in food formulation and food quality control.

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