Prediction of pH in Complex Aqueous Mixtures Using a Group-Contribution Method

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Expressions that suitably describe the behavior of weak electrolytes in aqueous systems are developed. A new numerical procedure is presented to allow for partial dissociation phenomena and so consider the whole species in solution. It is based on mass balances, the electroneutrality assumption, and dissociation constants of electrolytes. Combining it with a modified UNIFAC electrolyte group-contribution model based on the solvation concept directly allows calculation of pH, activities, and concentrations of species. The validity and usefulness of the expressions are tested using data for the pH of buffer solutions and complex aqueous mixtures such as fermentation media and liquid foods: pH values accurate to within ±0.05 pH units were obtained.

Introduction

Design and scale-up of reliable unit operations in the chemical and biochemical industries requires a thorough understanding of the complex mixtures involved. Species as diverse in size and molecular behavior as water, organic acids, bases, electrolytes, amino acids, nucleic acids, and metabolites occur together in cell extracts and fermentation broths, and modeling their interactions and phase equilibria behavior is difficult.

Recent work on the solution behavior of aqueous electrolyte systems has afforded several models for the excess Gibbs energy and electrolyte activity coefficients, including those of Pitzer (1973, 1980), Cruz and Renon (1978), Chen et al. (1982), Christensen et al. (1983), Ball et al. (1985), Chen and Evans (1986), Sander et al. (1986a,b,c), Macedo et al. (1990), Kikic et al. (1991), and Haghtalab and Vera (1988, 1989, 1991). These models are useful tools to calculate thermodynamic properties of salt-water or mixed salt-mixed solvent mixtures.

Some applications to electrolyte systems, in which the extent of dissociation of a weak electrolyte varies with pH, have been also proposed in the literature. Beutier and Renon (1978) and Edwards et al. (1978) characterized vapor-liquid equilibria for the ammonia-water and carbon dioxide-water systems. They combined dissociation properties with a semi-empirical expression for activity coefficient calculations composed of a Debye-Hückel term and a virial expansion.

Later, Nass (1988) correlated amino acid activity coefficients and solubility data, assuming the activity coefficient to be a product of terms for chemical reaction equilibrium and for physical interaction. Wilson's equation (Wilson, 1964) was used for the physical activity coefficient, with Bondi's volumes (Bondi, 1968) inserted for the pure-component liquid volume ratios. Activity coefficients for alanine, serine, and threonine in water and solubilities of phenylalanine, tyrosine, and diiodotyrosine in water were correlated.

Gupta and Heidemann (1990) extended this work to antibiotics, using the UNIFAC group-contribution method to calculate activity coefficients. They assumed no ionization of amino acids, and the solution is assumed to behave ideally for the expression of equilibrium constants and pH estimation. Activity coefficients are accordingly used only in the calculation of solid-liquid equilibrium properties.

Meyssami et al. (1992) estimated activity coefficients with different models according to the nature of the species. For molecular and ionic species, they used UNIFAC (Fredenslund et al., 1975) and Pitzer (Pitzer, 1973) equations respectively. Aqueous systems such as water-CO_2, water-citric acid-CO_2, and water-ascorbic acid-CO_2 were correlated by introducing activity coefficients into equilibrium relations. For these applications, the authors wrote systems of equations based on mass balances and equilibrium relations.

Many attempts to describe thermodynamic properties of partially dissociated aqueous systems have produced specific studies for particular aqueous solutions. However, as mentioned by Gal et al. (1989), mixtures are often assumed to be ideal, leading to weak approximations of pH even at low concentrations.

The objective of the work reported here was to develop and validate a generalized numerical procedure, particularly suitable for the calculation of real species concentrations and activities, and of pH in complex aqueous mixtures where many species may dissociate either partially or completely. To allow for nonideality of aqueous mixtures, this procedure was associated with a thermodynamic model specially developed to represent different types of interactions in aqueous solutions. Attention was focused on the prediction of pH in complex aqueous mixtures, for example, fermentation media and liquid foods.

Thermodynamic Framework

The dissociation of electrolytes in water generates new species, neutral, or ionized. Water itself is weakly ionized to H^+ and OH^- ions. Charged species not initially present in the mixture are produced, along with new electrostatic forces in the form of long-range interactions between species. To understand and predict the behavior of such systems, dissociation phenomena have therefore to be considered. The dissociation of weak electrolytes depends on pH; low pH values correspond to preponderant acid forms (for example, COOH and NH_3^+ groups), while forms such as COO^- and NH_2 predominate at high values of pH.

Here, we shall present and discuss successively: a thermodynamic model developed to allow for nonideality of aqueous systems, an automatic procedure to determine the number and nature of various species occurring in complex multicomponent aqueous solutions, allowing for dissociation phenomena, and equations associated with chemical theory developed to calculate activity coefficients, concentrations of species, and pH simultaneously using the thermodynamic model developed.

Features of the activity coefficient model

The thermodynamic properties of mixtures depend on the forces at play among the species in solution. Aqueous mixtures are characterized by three main kinds of interactions: physical interactions which result mainly from the dispersion forces (enthalpic effect) and from differences in size and shape (entropic effect) between molecules (Prausnitz et al., 1986), chemical interactions which arise through the chemical properties of particular groups inside molecules; they result in association and solvation phenomena when the separation distance between molecules is moderate (Acree, 1984), and electrostatic interactions which are due to the electric charges on ionic species resulting from dissociation of electrolytes (Robinson and Stokes, 1955).

Electrostatic forces are inversely proportional to the square of the separation distance (long-range), unlike other intermolecular interactions that depend on higher negative powers (short-range). Long-range forces dominate over dilute electrolyte concentrations. Hence, aqueous electrolyte solutions display marked nonideal behavior even when dilute. Conversely, short-range forces become preponderant at high electrolyte concentrations, resulting in strongly nonideal mixtures as all three kinds of interactions become important.

A new predictive model based on the solvation concept was developed in previous work to allow for short- and long-range interactions, and validated for the correlation and prediction of salt activities in aqueous and aqueous-solvent systems (Achard et al., 1994a,b). Below are described the main features of this model: for completeness, essential relations required for calculations in this work are reported in the Appendix. g^E (or equivalently the dimensionless excess Gibbs energy g^E/RT) is assumed to be the sum of two terms, one for short-range interactions (physical forces, solvation phenomena between water and ionic species), and the other for long-range electrostatic interactions.

$$\frac{g^E}{RT}=\frac{g^{E,SR}}{RT}+\frac{g^{E,LR}}{RT} \tag{1}$$

where superscripts *SR* and *LR* refer respectively to short- and long-range interactions; similarly for activity coefficients:

$$\ln\gamma_i=\ln\gamma_i^{SR}+\ln\gamma_i^{LR} \tag{2}$$

The short-range contribution combines the modified UNIFAC group-contribution model as proposed by Larsen et al. (1987) with solvation equations derived from chemical theory, for chemical interactions between water and ionic species. Solvation equation are based on the definition of a hydration number for each ion, which corresponds to the number of water molecules assumed to be chemically bound to charged species. Solvation phenomena are assumed to be constant with temperature and ionic strength. Thus, structural parameters of solvated species, mole fractions, that is, the true composition on the solution, and activity coefficients corresponding to short-range interactions are calculated by considering solvation phenomena. The calculation of γ_i from chemical theory and the equations developed are detailed elsewhere (Achard, 1992; Achard et al., 1994a).

The extended form of the Debye-Hückel equation proposed by Pitzer (1973, 1980) was adopted for long-range interactions, since the true mole fraction of all the species present, including ions, is used as the measure of composition, and since the equation gives some recognition to the repulsive forces between ions. Also, it has been successfully applied to aqueous strong electrolyte solutions by Chen et al. (1982).

The model, termed the modified UNIFAC electrolyte model, was applied to aqueous electrolyte solutions containing one or more completely dissociated salts for molalities up to 6 mol/kg. All applications have shown the model to be reliable and provided accurate calculations of thermodynamic properties such as the activity of water, mean activity coefficients of electrolytes, osmotic coefficients, boiling, and freezing points. Its characteristics allow predictive calculations in multielectrolyte aqueous mixtures and reliable extrapolation to unknown systems. UNIFAC group interaction parameters between water and ionic species, such as ionic hydration numbers, are available for 43 different ions derived from strong electrolytes (Na^+, Mg^{2+}, NO_3^-, Cl^-, and so on).

Automatic identification of species in complex aqueous mixtures

Principle. The processing of aqueous mixtures requires the complete characterization of species occurring in the solution. The first step is to determine what species are present in the mixture given the initial components. For example, when Na_2HPO_4 is dissolved in water, species Na^+, H^+, OH^-, PO_4^{3-},

HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4 will all be present in solution and will therefore have to be considered.

A special automatic procedure was developed to allow for dissociation phenomena in weak electrolytes, that is, organic or inorganic weak acids and bases, salts obtained from an acid/base pair, amino acids. This numerical procedure works like a database with structured relations between species. Ionization reactions can be predicted for every weak electrolyte. The function of the proposed procedure is to recognize these reactions in aqueous solutions automatically and identify the resulting species.

Certain specific problems arise:

- Uncharged species are not conserved; for example, when sodium acetate is dissolved in water, it gives species Na^+, CH_3COO^- and CH_3COOH, but no CH_3COONa.
- Ionic species are not always conserved in water; the addition of Na_2HPO_4, that is, Na^+ and HPO_4^- ions, in fact generates species Na^+, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4.
- If we consider a water-alcohol mixture, there is only one way to obtain a defined composition; this is not so with electrolyte mixtures; several water-acid-base-salt systems can be used to obtain a defined mixture. For example, a mixture containing set concentrations of Na^+ and CH_3COO^- ions can be obtained not only from sodium acetate, but also from a mixture of sodium hydroxide and acetic acid. This is one of the main reasons why previous work has always been on specific systems containing at most two or three electrolytes.

A thorough examination of systems to be described led to use as the reference mixture a hypothetical mixture composed exclusively of acids and bases rather than salts, acids, and bases. In any electrolyte, ionic species arising from dissociation phenomena always have an associated acid or base (Na^+: NaOH; Cl^-: HCl; PO_4^{3-}: H_3PO_4, ...). Also, salts are always composed of ions resulting from the combination of acids and bases. The two defined initial and reference mixtures have equivalent composition. Thus whatever the initial description of the mixture, it is converted to the corresponding reference mixture.

This approach allows simpler processing of electrolyte systems and effectively identifies true species: the number and nature of species liable to be formed by dissociation reactions are determined easily from reference acids and bases. It is also possible to determine the true mixture with the initial solution defined. However, the calculation of concentrations and activities in complex mixtures is difficult. With a mixture composed exclusively of acids and bases, this operation is simplified because equilibrium constants for dissociation reactions involving acids and bases are available in the literature. This special procedure affords two essential items of information: (i) the composition of the reference mixture, and (ii) species potentially occurring in solution. These will be subsequently used to calculate concentrations and activities of species.

Organization of Relations Between Components. The principle for establishing reference and true mixtures is shown in Figure 1. A system composed of water, acids, bases, salts, and nondissociable molecular species (solvents, polyols, saccharides, and so on) is initially defined.

The first step is an analysis of the ionic composition of electrolytes, acids, bases, and salts, giving what we term a primary mixture. To each one is associated its stoichiometric decomposition into ionic species:

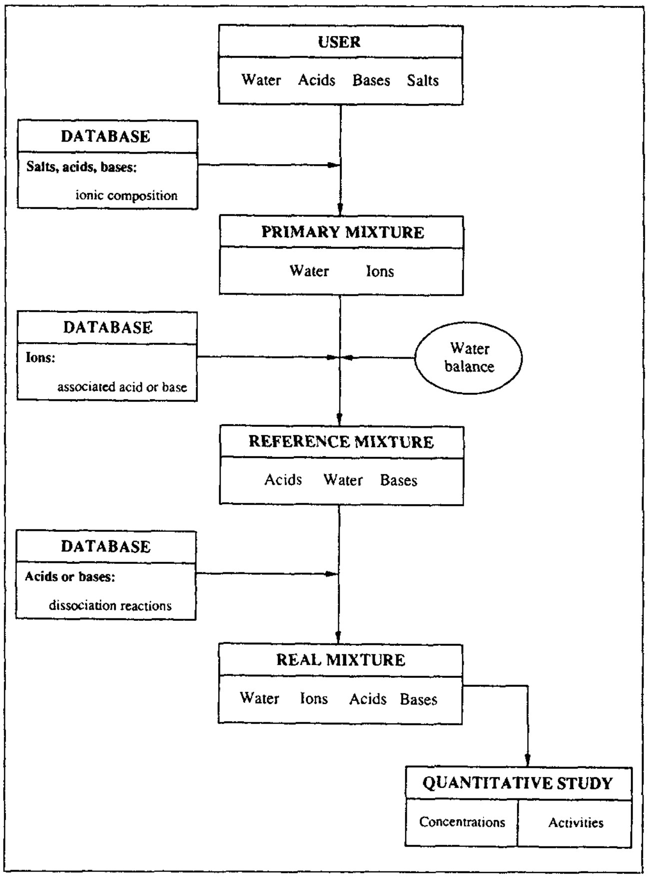

Figure 1. Overall scheme to establish reference and true mixtures.

$$C_{\nu c}A_{\nu a} \rightleftharpoons \nu_c C^{zc+} + \nu_a A^{za-} \tag{3}$$

For example, Na_2HPO_4, HCl, and NaOH correspond respectively to Na^+ and HPO_4^{2-}, H^+ and Cl^-, Na^+ and OH^-.

In the method, each ion is related to a reference component; this information is then used in a second step to establish the reference mixture from the primary one. When the identification number corresponds to a salt, this must be converted to equivalent acids and bases. However, for the composition to be respected, water molecules involved in these conversions have to be taken into account (1 mole NaCl corresponds to 1 mole HCl and 1 mole NaOH minus 1 mole water). The information necessary to perform such conversions must be stored in the database. To obtain a generalized procedure that works with any mixture, complex or simple, every possible case has to be considered. To include each component type, that is, amino acids, organic acids, and bases, CO_2, NH_3, we have associated with each ion stoichiometric coefficients *a* and *b* corresponding to the following reaction:

$$\text{Ion} \rightleftharpoons \text{reference component} + aH^+ + bOH^- \tag{4}$$

Some examples are shown in Table 1. Combining reactions 3 and 4 automatically gives the number of moles of water involved in the conversion from electrolyte to reference component. Thus, for Na_2CO_3, it corresponds to 2 moles of NaOH, 1 mole of CO_2, minus 1 mole of water.

Table 1. Relations between Ionic Species and their Reference Component According to Eq. 4

Ion	Reference Component	a H$^+$	b OH$^-$
Na^+	NaOH	0	−1
Cl^-	HCl	−1	0
NH_4^+	NH_3	+1	0
CO_3^{2-}	CO_2	−1	+1
$RCH(NH_2)COO^-$	$RCH(NH_3^+)COO^-$	−1	0
$RCH(NH_3^+)COOH$	$RCH(NH_3^+)COO$	+1	0

An acid or a base can be used as a reference for several ions, for example, H_3PO_4, but each ion must be associated with a single reference component to define the composition of the reference solution unambiguously. For ions corresponding to classical acids or bases (AH or BOH), there is no ambiguity in the definition of reference components.

Particular cases have to be taken into account:

- Carbonate and bicarbonate, like sulphide and bisulphide ions, have two possible reference components: CO_2 (or SO_2) and H_2CO_3 (or H_2SO_3); CO_2 and SO_2 are chosen as reference compounds instead of H_2CO_3 and H_2SO_3 of which concentrations in aqueous mixtures are close to zero. Hence, in the procedure presented here, the true concentration of H_2CO_3 in a solution containing HCO_3^-, CO_3^{2-}, and CO_2 is not determined, the two equilibria $CO_2 + H_2O \rightleftharpoons H_2CO_3$, and $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ being combined into $CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$.
- The same approach is used with NH_4^+ ions, which are generated in water by two different possible bases, a weak one (NH_3) and a strong one (NH_4OH). NH_3 is chosen as the reference compound; if NH_4OH is added in water, reaction 3 gives ions NH_4^+ and OH^-, and reaction 4 leads to NH_3; NH_4OH is therefore never present in the reference mixture. This choice of CO_2, SO_2, and NH_3 as reference compounds corresponds to the most realistic cases in engineering applications and directly provides gas-liquid equilibria involving multielectrolyte solutions.
- When amino acids are dissolved in water, they are almost completely converted to the zwitterion form and/or to one of the ions with a net charge; dissociation constants between zwitterion and uncharged amino acid are very large; this means that the amount of the uncharged amino acid in the aqueous solution is negligible and it is commonly assumed that amino acids occur mainly as the zwitterion and the net charged species; the zwitterion form is chosen as the reference component for amino acids; it is equivalent to the uncharged form.

The third step is the automatic determination of the true mixture from the reference, that is, the species potentially occurring in solution. Each reference compound is associated with ionic species given by dissociation reactions involving H^+ or OH^- ions. Examples of such dissociation reactions are given in Table 2.

Table 2. Ionization Reactions Involving H^+ or OH^- for Some Acids and Bases

Electrolyte CA	Ion 1	Ion 2	ν_1	ν_2
CH_3COOH	H^+	CH_3COO^-	+1	+1
CO_2	OH^-	HCO_3^-	−1	+1
	H^+	CO_3^{2-}	+1	+1
NH_3	H^+	NH_4^+	−1	+1
$RCH(NH_3^+)COO^-$	H^+	$RCH(NH_3^+)COOH$	−1	+1
	H^+	$RCH(NH_2)COO^-$	+1	+1
NaOH	OH^-	Na^+	+1	+1

As shown in Figure 1, information must be available to establish the reference and true mixtures. For each acid or base, ionization reactions with resulting ionic species have to be described and the equilibrium constants have to be known. For a salt, its ionic composition is needed and for ionic species, reference components have to be indicated.

Automatic calculations of pH, concentrations, and activities in complex aqueous mixtures

General Procedure. From information obtained earlier, that is, the number and nature of species and reference mixture composition, a generalized system of equations was developed to calculate activity coefficients and concentrations of species in complex aqueous mixtures simultaneously. This system is based on equilibrium relations, the electroneutrality assumption, and stoichiometric balances; it requires initial concentrations of water, acids, and bases, that is, composition of the reference mixture, as well as dissociation constants describing reactions.

For each acid/base pair, equilibrium relations between acid and base correspond to ionization reactions involving OH^- (basicity constant K_b) or H^+ (acidity constant K_a). For example, for the Na^+/NaOH pair, K_b and K_a are associated respectively with the following reactions $NaOH \rightleftharpoons Na^+ + OH^-$, and $Na^+ + H_2O \rightleftharpoons NaOH + H^+$. These two constants are related by:

$$\frac{K_a}{K_b} = K_w \tag{5}$$

where K_w is the dissociation constant of water. To simplify notations and develop generalized systems of equations, we shall refer in the following discussion to acidity constants K_a. Acids and bases can be split into four groups (reference components are underlined):

$$\begin{array}{llll} \underline{AH} & \rightleftharpoons A^- + H^+ & (CH_3COOH, \ldots)\ AH/A^- & (6a) \\ \underline{A} + H_2O & \rightleftharpoons AOH^- + H^+ & (CO_2, SO_2, \ldots) \quad A/AOH^- & (6b) \\ B^+ + H_2O & \rightleftharpoons \underline{BOH} + H^+ & (NaOH, \ldots) \quad B^+/BOH & (6b) \\ BH^+ & \rightleftharpoons \underline{B} + H^+ & (NH_3, \ldots) \quad BH^+/B & (6d) \end{array}$$

Acidity constants for strong acids are very large, and are close to zero for strong bases such as NaOH, implying that the NaOH concentration is negligible. It must be kept in mind that for acids such as CO_2 or bases such as NaOH, these reactions produce or consume water molecules. For example, when a mole of NaOH and a mole of HCl are added in water, a mole of OH^- is neutralized by a mole of H^+ to give an equivalent amount of water.

Thermodynamic equilibrium constants, K_a, are expressed as activity ratios. They remain constant for any composition at fixed T, P conditions. However, such constants are not avail-

Table 3. Expressions of Ionization Constants K_a (Activity Ratio), $K_a(c)$ (Concentration Ratio), and Relations Between $K_a(c)$ and $K_a^{id}(c)$ by Class of Electrolyte

Class of Electrolyte	K_a (–)	$K_a(c)$ (mol/l)	$K_a(c) = f(K_a^{id}(c))$
Acid			
No Water Consumed	$\frac{(\overset{*}{\gamma}_{H^+} x_{H^+})(\overset{*}{\gamma}_{A^-} x_{A^-})}{(\overset{*}{\gamma}_{AH} x_{AH})}$	$\frac{c_{H^+} c_{A^-}}{c_{AH}}$	$K_a(c) = \frac{v_w^{oL}}{v_m^L} \frac{\overset{*}{\gamma}_{AH}}{\overset{*}{\gamma}_{H^+} \overset{*}{\gamma}_{A^-}} K_a^{id}(c)$
Water Consumed	$\frac{(\overset{*}{\gamma}_{H^+} x_{H^+})(\overset{*}{\gamma}_{AOH^-} x_{AOH^-})}{(\overset{*}{\gamma}_A x_A)(\gamma_w x_w)}$	$\frac{c_{H^+} c_{AOH^-}}{c_A}$	$K_a(c) = \frac{v_w^{oL}}{v_m^L} \frac{\overset{*}{\gamma}_A}{\overset{*}{\gamma}_{H^+} \overset{*}{\gamma}_{AOH^-}} a_w K_a^{id}(c)$
Base			
No Water Produced	$\frac{(\overset{*}{\gamma}_{H^+} x_{H^+})(\overset{*}{\gamma}_A x_A)}{(\overset{*}{\gamma}_{AH^+} x_{AH^+})}$	$\frac{c_{H^+} c_A}{c_{AH^+}}$	$K_a(c) = \frac{v_w^{oL}}{v_m^L} \frac{\overset{*}{\gamma}_{AH^+}}{\overset{*}{\gamma}_{H^+} \overset{*}{\gamma}_A} K_a^{id}(c)$
Water Produced	$\frac{(\overset{*}{\gamma}_{H^+} x_{H^+})(\overset{*}{\gamma}_{AOH} x_{AOH})}{(\overset{*}{\gamma}_{A^+} x_{A^+})(\gamma_w x_w)}$	$\frac{c_{H^+} c_{AOH}}{c_{A^+}}$	$K_a(c) = \frac{v_w^{oL}}{v_m^L} \frac{\overset{*}{\gamma}_{A^+}}{\overset{*}{\gamma}_{H^+} \overset{*}{\gamma}_{AOH}} a_w K_a^{id}(c)$
Water	$\frac{(\overset{*}{\gamma}_{H^+} x_{H^+})(\overset{*}{\gamma}_{OH^-} x_{OH^-})}{(\gamma_w x_w)}$	$c_{H^+} c_{OH^-}$	$K_w(c) = \left(\frac{v_w^{oL}}{v_m^L}\right)^2 \frac{a_w}{\overset{*}{\gamma}_{H^+} \overset{*}{\gamma}_{OH^-}} K_w^{id}(c)$

able in the literature. Values of K_a in the literature correspond to concentration ratios and are determined experimentally near infinite dilution for a solution assumed to be ideal. They remain constant if the mixture behaves ideally and in practice for very dilute mixtures. In real systems, concentration ratios change with composition except near infinite dilution. To perform accurate calculations for true electrolyte mixtures, equilibrium constants have to allow for solution nonideality, that is, use activities of species.

The expression of acidity constants for the different types of ionization previously described are given in Table 3. True thermodynamic constants are denoted K_a and are dimensionless. They correspond to an infinite dilution standard state for solutes, that is, acids, bases, ionic species, and a pure liquid standard state for water. The mole fraction scale for activity coefficients is adopted; superscript * refers to an asymmetric convention for solute. Concentration ratios corresponding to pseudo-constants are denoted $K_a(c)$. They remain constant in ideal mixtures; in that particular case they are noted $K_a^{id}(c)$. Values of $K_a^{id}(c)$ are generally available in the literature (Patai, 1969; Rappoport, 1967; Sober et al., 1968; Weast, 1973; Lide, 1991). A classical approach is to solve a system of equations using $K_a^{id}(c)$ and $K_w^{id}(c)$, which gives concentrations of species corresponding to an ideal mixture. Similarly, pH^{id} is given by:

$$pH^{id} = -\log_{10}(c_{H^+}) \tag{7}$$

To improve calculations of c_i and pH, equilibrium constants must refer to concentration ratios $K_a(c)$ corresponding to the true mixture composition. Expressions can be established between $K_i(c)$ and $K_i^{id}(c)$ corresponding to water, acids, and bases using activity coefficient calculations; they are given in Table 3. The novelty of this procedure is to substitute $K_i^{id}(c)$ by $K_i(c)$ in a system of equations to estimate true concentrations and correct for solution nonideality. Activity coefficients are estimated using the modified UNIFAC electrolyte model presented above. In practice, activity coefficients and concentrations cannot be calculated independently. First, the reference mixture composition and values of $K_a^{id}(c)$, and $K_w^{id}(c)$ are used to give ideal mixture concentrations. The values of the constants $K_a(c)$ are then recalculated using the expressions listed in Table 3. The concentrations of the ionic species present in the solution are then re-estimated with the same algorithm as previously (Figure 2). This procedure is continued until convergence. Five iterative steps are generally necessary to obtain a relative precision for pH of 10^{-4}. The pH is then determined allowing for solution nonideality.

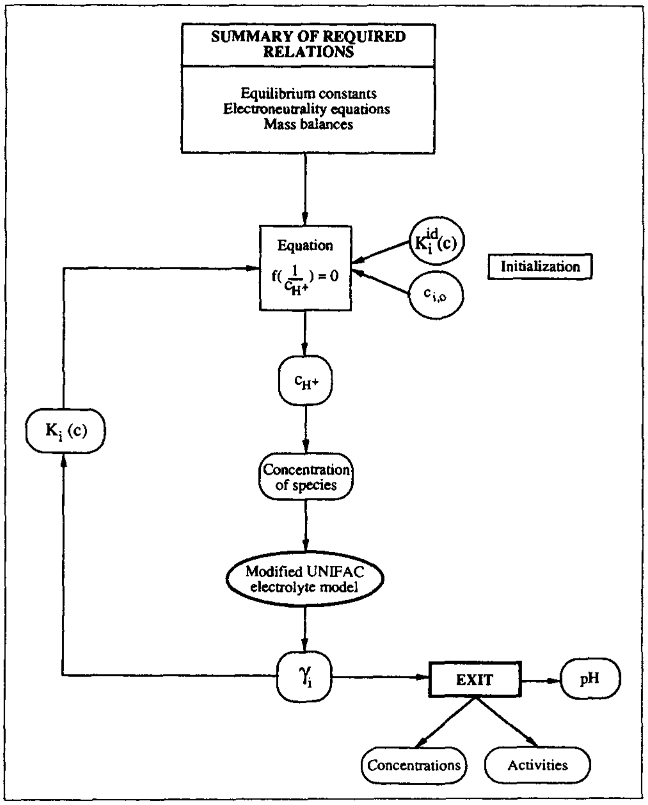

Figure 2. Overall scheme for simultaneous calculation of concentrations, activities, and pH.

$$\mathrm{pH}^a = -\log_{10}[\gamma^c_{\mathrm{H}^+} c_{\mathrm{H}^+}] \tag{8}$$

where $\gamma^c_{\mathrm{H}^+}$ is the activity coefficient of H^+ in a concentration scale. In the particular case of amino acids, electric charges located on zwitterion forms have to be considered because they affect the ionic strength of the mixture and modify long-range forces.

Automatic Calculation of the True Activities and Concentrations. The development of equations is first illustrated by a specific example, namely water-acetic acid. It will then be generalized to multicomponent mixtures. The following dissociation reaction is considered:

$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COO^-} + \mathrm{H^+} \tag{9}$$

Five species are present in the mixture: H^+, OH^-, $\mathrm{CH_3COOH}$, $\mathrm{CH_3COO^-}$, and $\mathrm{H_2O}$. OH^- ions are formed by ionization of water exclusively, but H^+ ions are generated by acetic acid as well as $\mathrm{H_2O}$.

Using the electroneutrality condition, mass balance equations and equilibrium properties, we can formulate the following system:

$$K_a(c) = \frac{c_{A^-} c_{\mathrm{H}^+}}{c_{ca}} \tag{10a}$$

$$K_w(c) = c_{\mathrm{H}^+} + c_{\mathrm{OH}^-} \tag{10b}$$

$$c_{\mathrm{H}^+} = c_{\mathrm{OH}^-} + c_{A^-} \tag{10c}$$

$$c_{ca,o} = c_{ca} + c_{A^-} \tag{10d}$$

$$c_{w,o} = c_w + c_{\mathrm{OH}^-} \tag{10e}$$

$c_{ca,o}$ and $c_{w,o}$ are initial concentrations of acetic acid and water (mol/l), and are given by the reference mixture composition. c_{A^-}, c_{H^+}, c_{ca}, c_{OH^-}, and c_w are the five unknown concentrations. The solution of the system of five Eqs. 10a to 10e yields the c_is. This type of nonlinear system can usually be solved using a Newton-Raphson method. However, the concentrations of the dissolved species may vary by several orders of magnitude (typically 14 orders of magnitude for c_{H^+} concentration). This introduces severe difficulties for automatic initialization and resolution of the system by classical numerical methods like the Newton-Raphson method. In addition, for complex aqueous solutions the number of species that dissociate may be large, thereby increasing the number of dimensions in the system. The method adopted in this work consists in reducing the system to a single-variable equation. As H^+ ions always occur in the solution, c_{H^+} was chosen as the key variable. Combination of Eqs. 10a and 10d gives:

$$c_{ca,o} = c_{ca}\left(1 + \frac{K_a(c)}{c_{\mathrm{H}^+}}\right) \tag{11}$$

Combining Eqs. 10a and 10c provides an expression for c_{H^+} concentration:

$$c_{\mathrm{H}^+} = \frac{K_w(c)}{c_{\mathrm{H}^+}} + c_{A^-} \tag{12}$$

From Eq. 12, the c_{H^+} concentration can be interpreted as the virtual sum of H^+ ions from water ($c_{\mathrm{H}^+}(w) = c_{\mathrm{OH}^-}$) and from acid dissociation ($c_{\mathrm{H}^+}(ca) = c_{A^-}$). Equations 11, 12, and 10d yield the final equation:

$$K_w(c)x^2 + c_{ca,o}x\left(\frac{K_a(c)x}{1 + K_a(c)x}\right) - 1 = 0 \tag{13}$$

where x is the inverse H^+ concentration $1/c_{\mathrm{H}^+}$. Equation 13 can be solved efficiently in the logarithm scale using the transformation $x = 10^{\mathrm{pH}}$. Any classical numerical technique can then be used to calculate pH from Eq. 13. Calculations of other concentrations are then performed using c_{H^+} with Eqs. 10a to 10e.

Whatever acid or base is considered, an expression similar to Eq. 13 can be developed. The generalization of this single-variable equation to multicomponent systems was undertaken. Considering the reference mixture where NC acids or bases are present, the N ionization reactions are characterized by their dissociation constants. Each component i ($i = 1$, NC) has NFA_i acid groups (giving H^+) and NFB_i basic groups (consuming H^+). For example, an amino acid contains both acid ($-\mathrm{COOH}$) and basic groups ($-\mathrm{NH_2}$). A general expression is established in the same way as Eq. 13 giving:

$$K_w^{id}(c)x^2 - 1 + \frac{\mathrm{Num}}{\mathrm{Den}} = 0 \tag{14}$$

with

$$\mathrm{Num} = \sum_{i=1}^{\mathrm{NC}} c_{i,0}x\left[\sum_{j=1}^{\mathrm{NFA}_i}\left(\nu_j j x^j \prod_{k=1}^{j} K_k\right) + \sum_{j=1}^{\mathrm{NFB}_i}\left(-\nu_j j x^{-j} \prod_{k=1}^{j} \frac{1}{K'_k}\right)\right]$$

$$\mathrm{Den} = \sum_{i=1}^{\mathrm{NC}}\left[1 + \sum_{j=1}^{\mathrm{NFA}_i}\left(x^j \prod_{k=1}^{j} K_k\right) + \sum_{j=1}^{\mathrm{NFB}_i}\left(x^{-j} \prod_{k=1}^{j} \frac{1}{K'_k}\right)\right]$$

where K_k and K'_k are acidity constants corresponding respectively to acid and basic groups. The resolution of Eq. 14 is performed as for Eq. 13. Generalized equations were established to calculate resulting concentrations c_i of other species. Concentrations of neutral components i $c_{i,n}$, that is, acids and bases, are calculated as follows:

$$c_{i,n} = \frac{c_{i,o}}{\mathrm{Den\,1}}$$

with

$$\mathrm{Den\,1} = 1 + \sum_{j=1}^{\mathrm{NFA}_i}\left[x^j \prod_{k=1}^{j} K_k\right] + \sum_{j=1}^{\mathrm{NFB}_i}\left[x^{-j} \prod_{k=1}^{j} \frac{1}{K'_k}\right] \tag{15}$$

Each acid or base i gives $\mathrm{NFA}_i + \mathrm{NFB}_i$ dissociation reactions in water, resulting in an equivalent number of associated ions. For reactions producing H^+, the expression for concentrations of ionic species is:

Table 4. Equilibrium Constants of Weak Electrolytes at 25°C (Patai, 1969; Rappoport, 1967; Weast, 1973; Sober et al., 1968; Lide, 1991)

Electrolyte	pK_1	pK_2	pK_3
Acetic acid	4.756		
Formic acid	3.750		
Gluconic acid	6.000		
Phosphoric acid	2.120	7.210	12.10
Lactic acid	3.860		
Malic acid	2.830	5.690	
Octanoic acid	4.890		
Oxalic acid	1.270	4.280	
Phtalic acid	2.950	5.408	
Propionic acid	4.874		
Tartaric acid	3.033		
Ascorbic acid	4.100	11.790	
Citric acid	3.128	4.761	6.39
CO_2	6.352	10.410	
NH_3	9.240		

Table 5. Structural Parameters of Neutral Groups (Larsen et al., 1987; DIPPR Tables, 1984)

Group	R_k	Q_k
H_2O	0.9200	1.400
CH_3	0.9011	0.848
CH_2	0.6744	0.540
CH	0.4469	0.228
C	0.2195	0.000
OH	1.0000	1.200
CH-O	0.6908	0.468
COOH	1.3013	1.224
NH_3	0.9096	0.980
CO_2	1.2986	1.292

$$c_j = x^j c_{i,n} \prod_{k=1}^{j} K_k \quad j = 1, \text{NFA}_i \tag{16}$$

and for NFB_i ions:

$$c_j = x^{-j} c_{i,n} \prod_{k=1}^{j} \frac{1}{K'_k} \quad j = 1, \text{NFB}_i \tag{17}$$

The value of c_{OH^-} is obtained from K_w and c_{H^+}. Calculation of c_w depends on dissociation reactions producing or consuming water molecules. Accordingly, it is calculated by a water balance on whole reactions. The quantity of H^+ produced or consumed is determined for each reaction. c_{H^+} is given by Eq. 14. The difference between these two quantities gives the number of moles of H^+ converted to water. The same calculation can be performed with OH^-.

Using the iterative procedure shown in Figure 2, the system at convergence gives activities, concentrations, and the pH of the true mixture. This procedure combined with an efficient activity coefficient model such as the modified UNIFAC electrolyte model should give access to several physicochemical properties of aqueous electrolyte solutions such as water activity, boiling and freezing points, osmotic properties, and energetic properties.

Correlation and Prediction of pH in True Aqueous Mixtures

The system defined by Eqs. 14 to 17 allows processing of every nonreacting aqueous mixture, even complex, when used in conjunction with the procedure shown in Figure 2. In the following examples, parameters required for calculations are given in Tables 4 to 8. Dissociation constants of weak electrolytes ($K_a^{id}(c)$) and structural parameters (R_k, Q_k) are obtained from literature sources. For the COO^- group, structural parameters are assumed to be equal to those of the COOH group. Group interaction parameters (a_{ij}) between solvent groups are the same as those published by Larsen et al. (1987). Hydration numbers (Nh_k) and group interaction energies (u_{ij}) involving ionic species have been fitted in a previous work to experimental data (Achard et al., 1994a,b). The a_{ij}s between solvent groups and ionized species are calculated from the u_{ij}s by the following relation:

Table 6. Parameters of the Model Involving Charged Species (R_k, Q_k: Weast, 1973; Bernard and Busnot, 1984; u_{ij}, Nh_k: Achard et al., 1994a,b)

Particle	R_k	Q_k	Nh_k	$u_{i,w}$ (K)	$u_{i,CH}$ (K)	$u_{i,OH}$ (K)
H^+	0.4661	0.6018	2.959	143.76	1,350.00	850.00
K^+	0.3910	0.5350	2.957	531.54	1,169.60	1,050.40
Na^+	0.1517	0.2847	2.606	401.50	1,381.00	829.00
NH_4^+	0.4862	0.6190	1.502	472.52	1,469.80	667.80
Ca^{2+}	0.1613	0.2967	3.077	−649.87	1,616.90	−353.20
Mg^{2+}	0.0478	0.1319	3.928	−589.56	1,791.20	−203.70
Cl^-	0.9860	0.9917	0.000	−1,054.00	2,500.00	−913.20
COO^-	1.3013**	1.2240**	0.000	0.00*	0.00*	0.00*
HCO_3^-	0.6313	0.7366	0.000*	0.00*	0.00*	0.00*
$H_2PO_4^-$	0.5784	0.6949	0.000	759.83	0.00*	0.00*
NO_3^-	0.9537	0.9699	0.476	−267.54	2,500.0	−541.90
OH^-	0.3912	0.5354	0.000	−1,302.46	2,500.0	−950.00
CO_3^{2-}	0.9379	0.9591	0.000*	0.00*	0.00*	0.00*
HPO_4^{2-}	0.5784	0.6949	0.000*	0.00*	0.00*	0.00*
SO_4^{2-}	2.8557	2.0149	0.000	−1,156.93	2,500.00	−1,201.90
PO_4^{3-}	0.5784	0.6949	0.000*	0.00*	0.00*	0.00*

* Parameters not yet available and set to zero.

** Assumed to be equal to structural parameters of COOH.

Table 7. Interaction Parameters between Solvent Groups at 298.15 K (Larsen et al., 1987)

a_{ij} (K)	H_2O	CH	OH	COOH	CH-O
H_2O	0.00	410.70	−47.15	−66.39	19.54
CH	1,857.00	0.00	972.80	664.10	230.50
OH	155.60	637.50	0.00	61.78	227.00
COOH	86.44	171.50	−92.21	0.00	−248.10
CH-O	183.10	369.90	137.10	286.60	0.00

Table 8. Group Interaction Energies u_{jj} between Like Groups (Achard et al., 1994a,b)

Group Interaction	u_{jj} (K)
Cation-cation	2,500.0
Anion-anion	2,500.0
Water-water	−700.0
Alkane-alkane	746.3
Alcohol-alcohol	−497.3

$$a_{ij} = u_{ij} - u_{jj} \tag{18}$$

Table 10. Comparison between Calculated pH Using Modified UNIFAC Electrolyte Model (pH^a) or Ideal Mixture Assumption (pH^{id}) and Experimental Data (Weast, 1973) in Binary Water Electrolyte Aqueous Solutions at 25°C

Component in Water	ΔpH^a	ΔpH^{id}	$\Delta pH^a/pH$ (%)	$\Delta pH^{id}/pH$ (%)
Acetic acid	0.010	0.023	0.328	0.843
Formic acid	0.050	0.090	2.174	3.913
Lactic acid	0.040	0.040	1.667	1.667
Citric acid	0.100	0.130	4.540	4.540
Malic acid	0.090	0.090	4.090	4.090
Tartaric acid	0.010	0.010	0.454	0.454
Oxalic acid	0.060	0.100	3.750	6.250
HCl	0.025	0.075	1.454	5.795
H_2SO_4	0.037	0.117	3.411	16.031
NaOH	0.086	0.103	0.653	0.790
KOH	0.080	0.103	0.604	0.790
NH_3	0.017	0.027	0.145	0.235
Na_3PO_4	0.010	0.470	0.083	3.920
Na_2CO_3	0.030	0.100	0.259	0.862
$NaHCO_3$	0.090	0.080	1.071	0.952
KH_2 citrate	0.076	0.169	2.013	4.476
Mean value	0.048	0.083	1.423	3.710

The u_{jj}s required for these calculations are reported in Table 8. Some remarks have to be pointed out: (i) interaction energies being not available were set equal to zero, (ii) aqueous concentrations of NH_3 and CO_2 were assumed to be very low and the a_{ij}s involving these gases were set to zero, (iii) for phosphate groups, structural parameters are only available for $H_2PO_4^-$; these values have been also used for other phosphate forms, and (iv) for H_2PO_4- group issued from the dissociation of a weak electrolyte, u_{ij} interaction energies should be fitted by considering dissociation reactions, and consequently the other existing forms (HPO_4^{2-}, PO_4^{3-}); however, data from Robinson and Stokes (1955) were given at low pH (acid medium); $H_2PO_4^-$ ion was then assumed to be preponderant and other forms to be quantitatively negligible.

The method and equations developed were tested and validated with pH data at 25°C. A comprehensive comparison was systematically made between experimental data and predictions in two cases, ideal and true. Values of pH obtained with mixed electrolyte mixtures are given in Table 9. Many of these are commonly used as buffer solutions (Weast, 1973). Notations pH^{exp}, pH^{id}, and pH^a refer respectively to experimental, ideal, and true values of pH. The results for several binary water-electrolyte mixtures are also listed in Table 10. The pH of mixtures assumed to be ideal can evidently differ widely from experimental values. ΔpH^{id} can reach up to 0.4 pH units, which is, in some cases, unacceptable. Values of pH^a calculated using the equations in Table 3 are systematically more accurate than pH^{id}; they correspond to mean relative deviations generally less than 1%, and absolute mean deviations never above 0.05 pH unit. Deviations observed in Table 10 are larger than with buffer solutions, and can be close to 0.1 pH unit. However, experimental values are approximate and must be used with caution (Weast, 1973). For strong bases such as NaOH or KOH, ΔpH is similar for ideal and true mixtures. However, pH^{id} is systematically larger than pH^{exp}, while pH^a is lower. This means that at high values of pH, between 12 and 14, solution nonideality is overcorrected.

Table 9. Comparison Between Calculated pH Using Modified UNIFAC Electrolyte Model (pH^a) or Ideal Mixture Assumption (pH^{id}) and Experimental Data in Mixed Electrolyte Aqueous Solutions at 25°C

System	ΔpH^{a*}	ΔpH^{id*}	$\Delta pH^a/pH^{**}$ (%)	$\Delta pH^{id}/pH^{**}$ (%)	Source
Water-NaOH-KCl	0.0082	0.107	0.066	0.857	Weast (1973)
Water-KCl-HCl	0.0265	0.117	1.768	7.945	Weast (1973)
Water-KH_2PO_4-NaOH	0.0109	0.336	0.167	4.880	Weast (1973)
Water-$NaHCO_3$-NaOH	0.0200	0.240	0.190	2.338	Weast (1973)
Water-Na_2HPO_4-KH_2PO_4	0.006	0.341	0.085	4.785	Weast (1973)
Water-acetic acid-sodium acetate	0.006	0.078	0.140	1.673	Weast (1973)
Water-citric acid-Na_2HPO_4	0.044	0.276	1.230	8.136	Laguerie et al. (1976)

$$^{*}\ \Delta pH(-) = \frac{1}{N}\sum_{i}^{N} |pH^{exp} - pH^{cal}|$$

$$^{**}\ \Delta pH(\%) = \frac{1}{N}\,\frac{\sum_{i}^{N} |pH^{exp} - pH^{cal}|}{pH^{exp}} \cdot 100$$

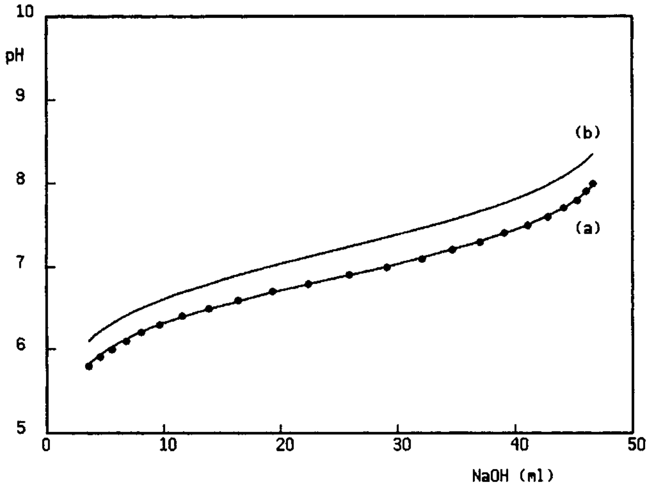

Figure 3. Comparison between calculated pH using modified UNIFAC electrolyte model (a) or ideal mixture assumption (b) and experimental data (Weast, 1973) in a KH_2PO_4 0.1 M, NaOH 0.1 M aqueous solution.

This discrepancy between pH^a and pH^{id} is mainly due to activity coefficients of ionic species, in particular $\gamma^*_{H^+}$ and $\gamma^*_{OH^-}$, that differ widely from 1 in the mixtures considered. All the systems in Tables 9 and 10 can be assumed to be dilute, and mainly exhibit long-range interactions between species. This results in lower values of ionic activity coefficients. Although interaction energies between solvent groups and carbonates or phosphates being not generally available, values of pH obtained with mixtures containing these species are accurate since the electrolytes are dilute ($c_i < 0.1$ mol/l) and short-range interactions can be neglected. The model described above gives representative values of activity coefficients due to electrostatic forces in aqueous dilute mixtures, without parameter fitting. The Pitzer-Debye-Hückel expression needs no adjustable parameters and calculates activity coefficients on the basis of ionic strength. This is also so for ionized functional groups derived from organic acids or amino acids (COO^-, NH_3^+) where no identification work has been performed to fit UNIFAC group interaction parameters between these groups and water. To determine thermodynamic properties of such systems up to the saturation curve, UNIFAC group interaction parameters must be available. However, fitting these parameters would require reliable data at high weak electrolyte concentration, which are generally scarce in the literature.

To illustrate the accuracy of the method, the predicted pH profile at 25 °C in standard aqueous buffer solutions containing KH_2PO_4 and NaOH is given in Figure 3. This clearly shows the high performance of the method.

It must be stressed that pH is represented satisfactorily if considered as the activity of H^+ (Eq. 8); no experimental value corresponding to single ion H^+ has been used when fitting UNIFAC group interaction parameters (Achard et al., 1993a,b). This confirms that the modified UNIFAC electrolyte model correctly predicts the activities of ionic species.

The mixtures processed so far are quite simple, being composed of three initial components at most. The procedure can be applied to more complex solutions encountered in industry. Values of pH predicted in fermentation media are reported in Table 11. *Corynebacterium melassecola* is a bacterium used industrially to produce amino acids. The medium, which is

Table 11. Comparison between Calculated pH Using Modified UNIFAC Electrolyte Model (pH^a), Ideal Mixture Assumption (pH^{id}), Pitzer Equation (pH^{PDH}), and Experimental Data in Fermentation Media at 25°C

Medium	Composition	Concentration (g/l)	pH^{exp}	pH^a	pH^{id}	pH^{PDH}
Basic medium for *Corynebacterium melassecola* without mineral salts and vitamins	Glucose	10.0	6.9	6.96	7.43	6.98
	$(NH_4)_2SO_4$	7.00				
	Na_2HPO_4	6.00				
	KH_2PO_4	3.00				
	NaCl	0.50				
	NH_2Cl	1.00				
Modified basic Zarrouk medium for *Spirulina platensis*	NaCl	1.00	9.7	9.63	10.16	9.61
	$CaCl_2$	0.03				
	K_2SO_4	1.00				
	$MgSo_4$, 7 H_2O	0.20				
	K_2HPO_4	0.50				
	$NaNO_3$	2.50				
	$NaHCO_3$	10.5				
	Na_2CO_3	7.60				
Medium for *Escherichia coli*	Glucose	10.0	7.0	7.06	7.46	7.08
	K_2HPO_4	7.00				
	KH_2PO_4	3.00				
	NH_4Cl	1.00				
	$MgSO_4$	0.10				
Medium for *Aspergillus niger*	Sucrose	30.0	5.65	5.69	5.69	5.95
	Yeast extract	1.00				
	$NaNO_3$	2.00				
	KCl	0.50				
	K_2HPO_4	1.00				
	$MgSO_4$	0.50				
	$CaCl_2$, 7 H_2O	5.50				

Table 12. Comparison between Calculated pH Using Modified UNIFAC Electrolyte Model (pH^a) or Ideal Mixture Assumption (pH^{id}) and Experimental Data (Meyssami et al., 1992) in Model Liquid Food Systems at 32°C

Components in Water	ΔpH^a	ΔpH^{id}	$\Delta pH^a/pH$ (%)	$\Delta pH^{id}/pH$ (%)
CO_2	0.02	0.03	0.579	0.866
CO_2-citric acid	0.03	0.06	0.916	1.674
CO_2-ascorbic acid	0.03	0.03	0.869	0.869
CO_2-citric acid-ascorbic acid	0.02	0.02	0.763	0.763
Mean value	0.026	0.033	0.778	0.987

described in Table 11, must be supplemented after sterilization with vitamins and mineral salts for bacteria to grow. *Spirulina platensis* is a photosynthetic microorganism yielding edible biomass. Modified Zarrouk medium is used to set ionic strength, and ensure bacterial growth. The carbon source is provided by CO_3^{2-} and HCO_3^- ions. Cultures of *Escherichia coli* are quite easy to grow with a simple medium. *Aspergillus niger* is an industrial microorganism used to produce citric acid or aromas. The composition given corresponds to a growth medium where substrate has to be added to give aroma. In every case, values of pH indicated in this table were obtained before sterilization. Close agreement is observed between experimental and predicted pH^a values. Absolute deviations are approximately 0.05 pH unit against 0.4 with pH^{id}, corresponding to relative deviations of less than 1%. This clearly shows the usefulness of this approach. For the *Aspergillus niger* medium, it has been shown experimentally that yeast extract addition does not modify the pH, and so this was not taken into account in the prediction of pH. Also, the pH value obtained with the composition given in Table 11 would be about 8. However, when Ca^{2+} ions are added, these react with HPO_4^{2-} ions and precipitate out, lowering the pH value to 5.65. As the procedure described cannot yet predict such phenomena, the pH is calculated by deleting HPO_4^{2-} ions and an equivalent quantity of Ca^{2+}. Values of pH calculated with the Pitzer equation are also given in Table 11 (pH^{PDH}). Differences with pH obtained using the modified UNIFAC electrolyte model are about 0.02 pH unit, except with medium for *Aspergillus niger* where ΔpH is about 0.26 pH unit. This comparison shows obviously that the use of UNIFAC and solvation equations provides a reasonable first-order correction.

The procedure was extended to the calculation of pH in model liquid food systems pressurized with carbon dioxide (water-CO_2, water-ascorbic acid-CO_2, water-citric acid-CO_2 and water-citric acid-ascorbic acid-CO_2 systems). Data were determined experimentally at 32°C by Messami et al. (1992) to predict the pH of orange juice and other liquid food systems under pressurized CO_2. Some results are shown in Table 12. As the vapor-liquid equilibrium properties of CO_2 coupled with its dissociation in water are not yet fully available with the selected method, the correlation of Wilhelm et al. (1977) was used to estimate solubility of CO_2 in pure water at 32°C in the range of Henry's law under CO_2 partial pressure of 1, 6.8, and 13.6 atm. In every case, predicted pH values are accurate; absolute deviations are less than 0.03 pH unit (relative deviation less than 1%).

Prediction of pH in industrial liquid food systems is possible if the exact composition is known. pH values of two food drinks are reported in Table 13. Predicted values are less accurate than the other calculations performed here. This loss of accuracy is attributed to approximate values for composition.

Table 13. Comparison between Calculated pH Using Modified UNIFAC Electrolyte Model (pH^a) or Ideal Mixture Assumption (pH^{id}) and Experimental Data in Liquid Foods at 25°C

Product	Composition	Conc. (g/L)	pH^{exp}	pH^a	pH^{id}
Flavored drink with tea aroma	Sugar (glucose)	75.0	3.08	2.96	2.91
	Citric acid, 1 H_2O	1.63			
	Sodium citrate	0.15			
	Maltodextrin (maltose)	0.80			
	Tea and aroma	traces			
Energizing drink	Total sugars (glucose-sucrose-fructose)	(mmol/L) 231.9	8.5	8.30	8.30
	NaCl	11.98			
	Magnesium lactate	0.618			
	Calcium bicarbonate	2.005			
	Potassium gluconate	0.854			

Conclusion

In this work is proposed a new simple generalized method to predict the real behavior of electrolyte aqueous systems. This is applicable to multicomponent aqueous mixtures where multiple dissociation phenomena may occur. It combines the electroneutrality assumption, mass balances, and dissociation constants of acids and bases, with a modified UNIFAC electrolyte model. This method affords pH of solutions, real concentrations, and activities of species. It gives accurate predictions of pH of buffer solutions, and of complex aqueous mixtures such as fermentation media and liquid food systems. Absolute deviations are overall less than 0.05 pH unit. Mixtures handled in this article are always given at low concentrations; the use of UNIFAC and solvation equations to calculate activity coefficients provides a reasonable first-order correction.

To extend this procedure to concentrated aqueous electrolyte mixtures, UNIFAC group interaction parameters between water and weak electrolyte specific groups ($-COOH$, $-NH_2$) have to be fitted; this implies having reliable data at high concentrations for such systems. However, in this work, the use of UNIFAC and solvation represents an attractive first estimate technique for those aqueous systems which contain organic acids, amino acids, nucleic acids, and other metabolites. The proposed-methodology might be a useful tool for engineering and industrial applications and for process simulation, since any nonreacting aqueous mixture composed of acids, bases, salts, sugars, and organic solvents at low concentrations can be successfully processed.

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Notation

a_i = activity
a_{ij} = UNIFAC binary group interaction parameter, K

A_{wk} = van der Waals surface area, cm^2/mol
c_i = concentration, mol l^{-1}
d = liquid density, g·cm^{-3}
D = dielectric constant of solvent i
e = electron charge, $4.802654 \cdot 10^{-10}$ e.u.
g = molar Gibbs energy, J·mol^{-1}
I_x = ionic strength on a mol fraction basis
k = Boltzman constant, $1.38048 \cdot 10^{-16}$ erg/K
K_a = acidity constant
K_b = basicity constant
K_i = equilibrium constant of ionization defined as activity ratio
$K_i(c)$ = equilibrium constant of ionization defined as concentration ratio, mol l^{-1}
M = molecular weight, g·mol^{-1}
N_A = Avogadro's number, 6.0225 mol^{-1}
NFA$_i$ = number of acid groups on electrolyte i
NFB$_i$ = number of basic groups on electrolyte i
Nh_i = hydration number of ion i at infinite dilution
pH = potential of hydrogen ion
P = pressure, atm
Q_k = relative van der Waals surface area of subgroup k
R = universal gas constant
R_k = relative van der Waals volume of subgroup k
T = temperature, K
u_{ij} = UNIFAC group interaction energy, K
v_i = molar volume, l mol^{-1}
V_{wk} = van der Waals volume, cm^3/mol
x_i = mol fraction
z_i = absolute value of ionic charge

Greek letters

γ_i = activity coefficient of component i
θ_i = surface area fraction of component i in mixture
ρ = closest approach parameter of the Pitzer expression
ν = electrolyte stoichiometric coefficient
$\nu_k^{(i)}$ = number of groups k present in molecule i
Φ_i = volume fraction of component i in mixture

Subscripts

a = anion
c = cation
ca = electrolyte CA
m = mixture
n = neutral species
o = initial conditions
s = solvent
w = water

Superscripts

$*$ = asymmetric convention
a = true mixture
c = molar concentration scale
C = combinatorial function
E = excess quantity
exp = experimental quantity
H = hydrated standard state
id = ideal mixture
L = liquid phase
LR = long-range contribution
o = pure substance
R = residual function
SR = short-range contribution

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Appendix

Group-contribution expression for short-range interactions

The selected model is here the modified form of the UNIFAC equation proposed by Larsen et al. (1987). For a mixture of N components, the combinatorial contribution to the activity coefficient is given by:

$$\ln \gamma_i^C = \ln\left(\frac{\Phi_i}{x_i}\right) + 1 - \frac{\Phi_i}{x_i} \qquad \text{(A1)}$$

with:

$$\Phi_i = \frac{x_i r_j^{2/3}}{\sum_j x_j r_j^{2/3}} \qquad \text{(A2)}$$

$$r_i = \sum_k \nu_k^{(i)} R_k \qquad \text{(A3)}$$

$$R_k = \frac{V_{wk}}{15.17} \qquad \text{(A4)}$$

$$Q_k = \frac{A_{wk}}{2.5\ 10^9} \qquad \text{(A5)}$$

The expression for the residual activity coefficient is:

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \qquad \text{(A6)}$$

with:

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \psi_{mk}\right) - \sum_m \left(\frac{\theta_m \psi_{km}}{\sum_p \theta_p \psi_{pm}} \right) \right] \qquad \text{(A7)}$$

$$\theta_m = \frac{Q_m X_m}{\sum_p Q_p X_p} \qquad \text{(A8)}$$

$$X_m = \frac{\sum_j \nu_m^{(j)} x_j}{\sum_j \sum_p \nu_p^{(j)} x_j} \qquad \text{(A9)}$$

$$\psi_{mn} = \exp\left[\frac{-(u_{mn} - u_{nn})}{RT}\right] = \exp\left[-\frac{a_{mn}}{RT}\right] \qquad \text{(A10)}$$

$\Gamma_k^{(i)}$ is also calculated with relations A7 to A10; the sums designed by subscript k, m, and p refer only to groups existing in a reference solution composed of molecule i.

Debye-Hückel expression for long-range interactions

In this work, the extended form of the Debye-Hückel equation proposed by Pitzer (1980) accounts for electrostatic forces. The relation for the activity coefficient is given by:

$$\ln \gamma_i^{*\mathrm{LR}} = -\left(\frac{1{,}000}{M_s}\right)^{0.5} A_\Phi \left[\left(\frac{2 z_i^2}{\rho}\right) \ln(1 + \rho I_x^{0.5}) + \frac{(z_i^2 I_x^{0.5} - 2 I_x^{1.5})}{(1 + \rho I_x^{0.5})} \right] \qquad \text{(A11)}$$

with:

$$A_\Phi = \frac{1}{3}\left(\frac{2\pi N_A d_s}{1{,}000}\right)^{0.5} \left(\frac{e^2}{D_s k T}\right)^{1.5} \qquad \text{(A12)}$$

$$I_x = \frac{1}{2} \sum x_i z_i^2 \qquad \text{(A13)}$$

$$D_s = -31.61 + \frac{32{,}733.43}{T} \qquad \text{(A14)}$$

A_Φ can be rewritten as $A_\Phi = 1.40\ 10^6 \sqrt{d_s}/(D_s T)^{1/5}$, and is expressed in $(\mathrm{g/mol})^{0.5}$.

Solvation equations

In what follows, notation H always refers to the hydrated standard state. Variables corresponding to the classical standard state have no superscript.

Structural Parameters of Hydrated Species

$$R_k^H = R_k + Nh_k R_1 \qquad \text{(A15)}$$

$$Q_k^H = Q_k + Nh_k Q_1 \qquad \text{(A16)}$$

where R_1 and Q_1 refer to water, and Nh_k represents the infinite dilution hydration number of k.

Mole Fractions Corresponding to the Hydrated Standard State. We consider a liquid mixture of N components where 1 is water. The other $N-1$ species may be solvated by water.

Mole fractions of water and ionic species are respectively:

$$x_1^H = \frac{x_1 - \sum_{J=2}^{N} Nh_J x_J}{1 - \sum_{J=2}^{N} Nh_J x_J} \tag{A17}$$

$$x_i^H = \frac{x_i}{1 - \sum_{J=2}^{N} Nh_J x_J} \tag{A18}$$

Analytical Relation Between γ_i^{SR} and $\gamma_i^{SR,H}$. Activity coefficients of water and ionic species are respectively:

$$\gamma_1^{SR} = \gamma_1^{SR,H} \frac{x_1^H}{x_1} \tag{A19}$$

$$\gamma_i^{SR} = \gamma_i^{SR,H} \frac{x_i^H}{x_i} [\gamma_1^{SR,H} x_1^H]^{-Nhi} \quad (i \neq 1) \tag{A20}$$

In practice, $\gamma_1^{SR,H}$ and $\gamma_i^{SR,H}$ are calculated with the modified UNIFAC equation (relations A1 to A10) using mole fractions and structural parameters of hydrated species. Relations A19 and A20 are then used to calculate γ_1^{SR} and γ_i^{SR}. The resulting activity coefficients are given by relation 2. It must be outlined that formulas A19 and A20 satisfy the Gibbs-Duhem fundamental equation.

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