Water Activity and pH in Aqueous Polycarboxylic Acid Systems

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Water activities and pH for binary and ternary aqueous systems with polycarboxylic acids (citric, malic, malonic, oxalic, succinic, and tartaric) were measured at 298.15 K. The solute concentration in binary systems varied from (5 to 50) mass % for citric, malic, malonic, and tartaric acids. For oxalic and succinic acids, which present low solubilities in water, the solute concentration varied from (2 to 10 and 1.5 to 5.5) mass %, respectively. In ternary mixtures the total acid concentration varied from (5 to 50) mass %. A modified UNIFAC group contribution model was used for predicting water activity and pH data. In the model formulation, a Pitzer−Debye−Hückel term was added to represent the electrostatic interactions between ionic species which arose from the partial dissociation of weak acids. The solvation phenomenon between water and ions was also considered. To take into account all species present in the mixture, a numerical procedure based on chemical equilibrium constants, the electroneutrality condition, and stoichiometric balances was associated with the modified UNIFAC model. The close agreement between measured and calculated data showed the high performance of the model, with an average deviation of 0.4% for water activity and 1.3% for pH.

Introduction

Polycarboxylic acids are biochemical compounds that occur extensively in food systems such as fruit juices, tomato paste, coffee extract, and fermented milk. In fruit juices they are mainly citric, malic, oxalic, and tartaric acids, depending on the kind of fruit. The presence of acids is responsible for the low pH values of fruit juices, which permits sterilization to be achieved under less severe thermal conditions and has the added advantage of preventing the growth of bacteria potentially dangerous to human health. Such compounds are also added for numerous purposes in food processing where they provide the benefits of many of their natural actions. Organic acids are commonly incorporated into foods to produce a sour taste and intensify the taste perception of other flavoring agents. They also play an important role in food stabilization by complexing metals that otherwise could promote oxidation of flavor compounds and catalyze discoloration reactions.[1−3]

Water activity (a_w) and pH are physicochemical properties of great importance in the food industry since the chemical and microbial stability of food is highly dependent on both a_w and pH values.[4] Experimental information and the development of predictive models for estimating these properties in food systems are consequently essential for designing and optimizing industrial processes such as evaporation, freeze concentration, and thermal sterilization.

Polycarboxylic acids are weak electrolytes with partial dissociation in aqueous systems. Group contribution-based models such as UNIFAC[5,6] and ASOG[7] have been successfully applied to calculate thermodynamic properties in food systems containing nonelectrolytes such as sugars,[8−14] poly(ethylene glycol)s,[15] and polyols.[11,16] However, up to now, much less attention has been given to partially dissociated aqueous systems. Achard et al.[17] proposed a generalized numerical procedure associated with a modified group contribution model to describe the behavior of weak electrolytes in water. Velezmoro and Meirelles extended this technique for estimating water activities in some binary aqueous systems containing weak acids[18] and organic salts.[19] Such a procedure was also used with success by Ninni et al.[20] for predicting water activities and pH of amino acids in aqueous and buffer systems.

The present paper may be separated into two parts. The aim of the first one was to measure water activities and pH for six kinds of binary aqueous systems containing one polycarboxylic acid (citric, malic, malonic, oxalic, succinic, or tartaric) and also for model lemon juice systems (represented here by ternary aqueous mixtures with citric and malic acids). In the second part of the study, water activities and pH were predicted considering the nonideality of these systems, by using a modified UNIFAC group contribution model combined with the numerical procedure already mentioned.[17] In the model formulation, a Pitzer−Debye−Hückel term[21] was added to represent the electrostatic interactions between ions resulting from the dissociation of electrolytes. The solvation phenomenon between water and ionic species was also considered. The model predictive capabilities were finally tested by using the experimental data obtained in the present work.

Experimental Section

Materials. The following polycarboxylic acids were used: citric, malic, malonic, oxalic, succinic, and tartaric acids. They were analytical grade reagents from Merck, with the exception of malic (Sigma) and malonic (Alfa Aesar) acids. All of them had purities higher than 99 mass %. The water used in making each solution was distilled and deionized with a Milli-Q device (Millipore−USA).

Experimental Procedure. Binary aqueous polycarboxylic acid mixtures were prepared by mass using an analytical balance (Sartorius Analytic−GmbH) with ±0.1 mg accuracy. The solute concentration varied from (5 to

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Table 1. Experimental Water Activities for Binary Mixtures at 298.15 K

water (1) + citric acid (2)			water (1) + malic acid (2)			water (1) + malonic acid (2)		
$w_2{}^a$	a_w	σ^b	w_2	a_w	σ^b	w_2	a_w	σ^b
0.0499	0.993	0.000	0.0499	0.994	0.001	0.0498	0.997	0.000
0.0995	0.987	0.001	0.0994	0.987	0.000	0.0997	0.986	0.001
0.1990	0.973	0.001	0.1986	0.966	0.000	0.1993	0.966	0.001
0.2987	0.954	0.001	0.3007	0.938	0.001	0.2989	0.935	0.000
0.3982	0.924	0.001	0.3982	0.900	0.003	0.3986	0.892	0.001
0.4948	0.874	0.001	0.4970	0.848	0.002	0.4983	0.827	0.000

water (1) + oxalic acid (2)			water (1) + succinic acid (2)			water (1) + tartaric acid (2)		
w_2	a_w	σ^b	w_2	a_w	σ^b	w_2	a_w	σ^b
						0.0504	0.993	0.001
0.0203	0.992	0.000	0.0149	0.995	0.000	0.1005	0.989	0.001
0.0401	0.989	0.000	0.0249	0.994	0.001	0.2001	0.975	0.001
0.0600	0.984	0.001	0.0350	0.993	0.001	0.3001	0.949	0.001
0.0801	0.980	0.001	0.0452	0.992	0.000	0.4041	0.907	0.000
0.1000	0.975	0.001	0.0546	0.991	0.000	0.4997	0.849	0.000

[a] Acid mass fraction. [b] Standard deviation of the experimentally measured water activity.

Table 2. Experimental pH Data for Binary Mixtures at 298.15 K

water (1) + citric acid (2)			water (1) + malic acid (2)			water (1) + malonic acid (2)		
$w_2{}^a$	pH	σ^b	w_2	pH	σ^b	w_2	pH	σ^b
0.0499	1.79	0.01	0.0502	1.89	0.03	0.0498	1.53	0.01
0.0995	1.56	0.01	0.0995	1.67	0.01	0.0997	1.35	0.01
0.1990	1.26	0.01	0.1989	1.37	0.01	0.1993	1.08	0.02
0.2987	1.03	0.01	0.2983	1.12	0.01	0.2989	0.83	0.01
0.3982	0.77	0.05	0.3978	0.86	0.01	0.3986	0.58	0.01
0.4948	0.50	0.00	0.4966	0.55	0.07	0.4983	0.33	0.01

water (1) + oxalic acid (2)			water (1) + succinic acid (2)			water (1) + tartaric acid (2)		
w_2	pH	σ^b	w_2	pH	σ^b	w_2	pH	σ^b
						0.0499	1.73	0.01
0.0203	1.08	0.02	0.0149	2.53	0.00	0.1000	1.48	0.00
0.0401	0.88	0.01	0.0255	2.41	0.02	0.2004	1.19	0.01
0.0600	0.76	0.01	0.0348	2.31	0.00	0.2969	1.01	0.01
0.0801	0.67	0.02	0.0447	2.26	0.01	0.3963	0.73	0.02
0.1000	0.59	0.01	0.0549	2.20	0.01	0.4886	0.54	0.01

[a] Acid mass fraction. [b] Standard deviation of the experimentally measured pH.

Table 3. Measured Water Activities and pH for Water (1) + Malic Acid (2) + Citric Acid (3) Mixtures at 298.15 K

$w_2{}^a$	$w_3{}^a$	a_w	σ^b	pH	σ^b
0.0059	0.0439	0.993	0.001	1.82	0.01
0.0119	0.0878	0.986	0.000	1.59	0.01
0.0236	0.1755	0.973	0.001	1.30	0.00
0.0355	0.2633	0.951	0.001	1.08	0.00
0.0473	0.3511	0.919	0.001	0.79	0.01
0.0590	0.4389	0.872	0.001	0.50	0.01

[a] Acid mass fraction. [b] Standard deviation of the experimentally measured data.

50) mass % for citric, malic, malonic, and tartaric acids. For oxalic and succinic acids, which present low solubilities in water, the solute concentration varied from (2 to 10 and 1.5 to 5.5) mass %, respectively. By a similar procedure, ternary aqueous mixtures with citric and malic acids were also prepared. Such mixtures are particularly important in fruit juice industries because they contain the major components of lemon juice. To simulate lemon juice systems, solutions of approximately 7:1 citric acid/malic acid ratio[22,23] were prepared, with total acid concentration between 5 and 50 mass %. Compositions of binary and ternary mixtures were accurate to ±0.01% approximately in mass percent. The water content in the solid polycarboxylic acids was previously determined by Karl Fischer titration (Metrohn−Swiss). The amount of water varied from (0.03 to 0.56) mass %, and it was considered for calculating the water concentration in each solution.

Water activities were measured at 298.15 K by an electronic hygrometer Aqua-Lab CX-2T (Decagon Device Inc.−USA) previously calibrated with saturated salt solutions. The temperature inside the equipment could be regulated within ±0.1 K by circulation of water from a thermostatic bath (Paar Physica−GmbH). Each water activity data point was taken as an average of three measurements. The mean standard deviation obtained for the whole set of experimental data was 0.001 a_w units.

Measurements of pH at the same temperature were carried out using a Chemcadet 5986-50 pH meter (Cole Parmer Instrument Co.−USA). Buffer solutions were used in the instrument calibration. During each measurement, samples were kept in a thermostatic liquid bath (Cole Parmer Instrument Co.−USA) at the desired temperature and controlled within ±0.1 K. Thermometers (H−B Inst. Co.−USA) with subdivisions of ±0.1 K were used for monitoring the bath temperature. Each pH data point was taken as an average of three measurements. The mean standard deviation obtained for the whole set of experimental data was 0.01 pH units.

Experimental water activity and pH data for binary aqueous polycarboxylic acid mixtures are summarized respectively in Tables 1 and 2. Measured water activities and pH for ternary mixtures are presented in Table 3. Polycarboxylic acid concentrations are expressed in mass fractions. Tables 1−3 also show the standard deviation for each experimental data point. As already pointed out in the experimental method description, both measured water activities and pH presented an excellent reproducibility. It should be mentioned that the electronic hygrometer method used here also provided an accurate water activity measurement for some binary weak acid and organic salt systems[18,19] and for mixtures with sugars, poly(ethylene glycol)s, polyols, and amino acids.[14−16,20]

Thermodynamic Analysis

Modified UNIFAC Model for Electrolytes. The original UNIFAC group contribution model[5] is a reliable and fast technique for estimating liquid-phase activity coefficients for nonelectrolytes. The activity coefficient is assumed to be the sum of a combinatorial and a residual contribution. The first one is due to differences in size and shape of the molecules in the mixture, so that only pure component properties are considered. The second contribution takes into account the energy of interaction between the different groups present in the mixture.

The UNIFAC model can be extended to electrolytes, like organic acids, by introducing the term of Pitzer based on the Debye−Hückel theory.[21] The activity coefficient is assumed to be the sum of a term for short-range (physical and chemical) interactions and another one for long-range (electrostatic) interactions:

$$\ln(\gamma_i) = \ln(\gamma_i^{\mathrm{SR}}) + \ln(\gamma_i^{\mathrm{LR}}) \tag{1}$$

where the superscripts SR and LR refer respectively to short- and long-range interactions.

Following a procedure similar to that proposed by Achard et al.,[17] the short-range contribution was calculated by the UNIFAC model combined with solvation equations for chemical interactions between water and ions. Structural parameters and mole fractions of hydrated species are calculated by considering the number of water molecules bound to ionic species. The group volume and surface area parameters are as follows:

$$R_k^{\mathrm{H}} = R_k + Nh_k R_1 \tag{2}$$

$$Q_k^{\mathrm{H}} = Q_k + Nh_k Q_1 \tag{3}$$

where the superscript H and the subscript 1 refer respectively to the hydrated state and water, and Nh_k is the hydration number of group k.

For a mixture with n components, the water mole fraction, considering the solvation of ions, and the mole fraction of ionic species are respectively:

$$x_1^{\mathrm{H}} = \frac{x_1 - \sum_2^n Nh_j x_j}{1 - \sum_2^n Nh_j x_j} \tag{4}$$

$$x_i^{\mathrm{H}} = \frac{x_i}{1 - \sum_2^n Nh_j x_j} \tag{5}$$

and the activity coefficients of water and the ionic species are respectively:

$$\gamma_1^{\mathrm{SR}} = \gamma_1^{\mathrm{SR,H}} \frac{x_1^{\mathrm{H}}}{x_1} \tag{6}$$

$$\gamma_i^{\mathrm{SR}} = \gamma_i^{\mathrm{SR,H}} \frac{x_i^{\mathrm{H}}}{x_i} (\gamma_1^{\mathrm{SR,H}} x_1^{\mathrm{H}})^{-Nh_i} \quad (i \neq 1) \tag{7}$$

The activity coefficients $\gamma_1^{\mathrm{SR,H}}$ and $\gamma_i^{\mathrm{SR,H}}$ were calculated with the UNIFAC model using structural parameters and mole fractions of hydrated species, and then eqs 6 and 7 were used for calculating γ_1^{SR} and γ_i^{SR}.

In the present work, the solvation phenomenon was considered for the ion H^+, since its hydration number (=2.959) was already available in the literature.[17] For the other ionic species (all anions), hydration number data are not yet available and were set to zero; that is, it was assumed that anions remain in a nonhydrated state. The mentioned assumption may be considered quite reasonable, since solvation of anions is in general significantly lower, compared to that of cations.[24,25] Consequently, it seems that such an assumption does not have a significant influence on the quality of the prediction.

In this work, the long-range contribution in eq 1 was represented by the Pitzer−Debye−Hückel expression for the activity coefficient.[21] The closest approach parameter of the Pitzer−Debye−Hückel equation was adjusted by Achard et al.[26] over phase equilibrium data for a large number of electrolyte systems, resulting in an optimal value of 17.1.

To take into account all the ionic species which arose from the partial dissociation of polycarboxylic acids, a numerical procedure, described in detail by Achard et al.,[17] had to be associated with the modified UNIFAC model presented above. Such a procedure requires the initial water and solute concentrations, as well as values of chemical equilibrium constants. It can be illustrated by the following example:

In an aqueous malic acid system, some dissociation reactions take place:

$$\mathrm{H_2Malic} \leftrightarrow \mathrm{H^+} + \mathrm{HMalic^-} \tag{8}$$

$$\mathrm{HMalic^-} \leftrightarrow \mathrm{H^+} + \mathrm{Malic^{2-}} \tag{9}$$

$$\mathrm{H_2O} \leftrightarrow \mathrm{H^+} + \mathrm{OH^-} \tag{10}$$

For simultaneous calculation of dissociated species concentrations and their activity coefficients in aqueous mixtures, a system of equations was developed. Using chemical equilibrium constants, the electroneutrality condition, and stoichiometric balances, the following system can be formulated:

$$K_1 = \frac{c_{\mathrm{H^+}} c_{\mathrm{HMalic^-}}}{c_{\mathrm{H_2Malic}}} \frac{\gamma^*_{\mathrm{H^+}} \gamma^*_{\mathrm{HMalic^-}}}{\gamma^*_{\mathrm{H_2Malic}}} \frac{v_{\mathrm{m}}^{\mathrm{L}}}{v_{\mathrm{w}}^{\mathrm{oL}}} \tag{11}$$

$$K_2 = \frac{c_{\mathrm{H^+}} c_{\mathrm{Malic^{2-}}}}{c_{\mathrm{HMalic^-}}} \frac{\gamma^*_{\mathrm{H^+}} \gamma^*_{\mathrm{Malic^{2-}}}}{\gamma^*_{\mathrm{HMalic^-}}} \frac{v_{\mathrm{m}}^{\mathrm{L}}}{v_{\mathrm{w}}^{\mathrm{oL}}} \tag{12}$$

$$K_{\mathrm{w}} = c_{\mathrm{H^+}} c_{\mathrm{OH^-}} \frac{\gamma^*_{\mathrm{H^+}} \gamma^*_{\mathrm{OH^-}}}{a_{\mathrm{w}}} \left(\frac{v_{\mathrm{m}}^{\mathrm{L}}}{v_{\mathrm{w}}^{\mathrm{oL}}} \right)^2 \tag{13}$$

$$c_{\mathrm{H^+}} = c_{\mathrm{OH^-}} + c_{\mathrm{HMalic^-}} + 2c_{\mathrm{Malic^{2-}}} \tag{14}$$

$$c_{\mathrm{o,H_2Malic}} = c_{\mathrm{H_2Malic}} + c_{\mathrm{HMalic^-}} + c_{\mathrm{Malic^{2-}}} \tag{15}$$

$$c_{\mathrm{o,H_2O}} = c_{\mathrm{H_2O}} + c_{\mathrm{OH^-}} \tag{16}$$

In these equations, K, c, $v_{\mathrm{m}}^{\mathrm{L}}$, and $v_{\mathrm{w}}^{\mathrm{oL}}$ are the chemical equilibrium constants ($\mathrm{mol \cdot L^{-1}}$), the species concentrations ($\mathrm{mol \cdot L^{-1}}$), the liquid mixture molar volume ($\mathrm{L \cdot mol^{-1}}$), and the molar volume for pure water, respectively. The superscript $*$and the subscript o refer respectively to an asymmetric convention for solute[27] and the initial concentration.

The activity coefficient γ_i^* can be calculated by eq 17 using the UNIFAC model:

$$\ln(\gamma_i^*) = \ln(\gamma_i) - \ln(\gamma_i^{\bullet}) \tag{17}$$

where γ_i^* is the asymmetric activity coefficient and $\gamma_i^{\bullet}$ is the activity coefficient at infinite dilution of all solutes in the mixture:

$$\gamma_i^{\bullet} = \lim_{x_{\mathrm{w}} \to 1} \gamma_i \tag{18}$$

where x_{w} is the water mole fraction.

Using the procedure presented above in conjunction with the modified UNIFAC model, the true concentrations of all species in solution and their activity coefficients could be simultaneously calculated by means of an iterative process. Chemical equilibrium constants for weak acids at 298.15 K were found in the literature[28] and are listed in Table 4. Molar volumes of aqueous organic acid mixtures were calculated from density data for these systems, which were measured from (293.15 to 323.15) K, and also correlated with temperature and acid concentration in previous work.[29]

Table 4. Chemical Equilibrium Constants (mol·L^{-1}) for Weak Electrolytes at 298.15 K

electrolyte	K_1	K_2	K_3
citric acid	7.45×10^{-4}	1.73×10^{-5}	4.02×10^{-7}
malic acid	3.48×10^{-4}	8.00×10^{-6}	
malonic acid	1.49×10^{-3}	2.01×10^{-6}	
oxalic acid	5.36×10^{-2}	5.42×10^{-5}	
succinic acid	6.21×10^{-5}	2.32×10^{-6}	
tartaric acid	9.20×10^{-4}	4.31×10^{-5}	

Table 5. Chemical Structures for Polycarboxylic Acids

polycarboxylic acid	structure
citric acid	$HOOCCH_2COH(COOH)CH_2COOH$
malic acid	$HOOCCHOHCH_2COOH$
malonic acid	$HOOCCH_2COOH$
oxalic acid	HOOCCOOH
succinic acid	$HOOCCH_2CH_2COOH$
tartaric acid	HOOCCHOHCHOHCOOH

Table 6. UNIFAC Groups and Structural Parameters for Polycarboxylic Acid Systems

group	subgroup	R_k	Q_k
COOH	COOH	1.3013	1.224
CH_2	CH_2	0.6744	0.540
	CH	0.4469	0.228
	C	0.2195	0.000
OH	OH	1.0000	1.200
COO^-	COO^-	1.3013	1.224
OH^-	OH^-	0.3912	0.535
H^+	H^+	0.4661	0.602
H_2O	H_2O	0.9200	1.400

UNIFAC Structural and Interaction Groups. The chemical structures for the weak acids focused on in this work are presented in Table 5. The UNIFAC main groups and subgroups for aqueous polycarboxylic acid systems, considering whole and dissociated species, as well as their structural parameters are summarized in Table 6. Volume and surface area parameters for nonionic groups were obtained from Gmehling et al.,[30] and those for ionic groups were found in ref 17.

Interaction parameters between polar groups (COOH, OH, and H_2O) were previously readjusted by Velezmoro,[31] since the original UNIFAC parameters generally do not predict well physicochemical properties for biochemical systems with multiple strongly polar groups in the same molecule.[32] The readjustment process was performed using water activity data for some binary weak electrolyte systems, and the estimated values were used here. Interaction parameters for the other nonionic groups were taken from Gmehling et al.[30] Parameters between nonionic and ionic groups and those involving only ionic groups were found in ref 17. It was attempted to estimate the parameters between the COOH group and the ionic ones (not available), and there was no significant improvement in the model performance. Hence, it was decided to set them equal to zero, following the suggestion presented by Achard et al.[17] Values for the group interaction parameters used in this work are presented in Table 7.

Prediction of Physicochemical Properties

The water activity, a parameter widely used to indicate the availability of water in food systems, is defined as the ratio of the water fugacity in a sample and the fugacity of pure water at the same temperature and pressure:[4]

$$a_w = \frac{f_w}{f_w^o} = x_w \gamma_w \tag{19}$$

where f_w and f_w^o are respectively the water fugacity in a sample and the fugacity of pure water at the reference condition.

At moderated temperature and pressure, the vapor phase behaves ideally and the fugacity ratio can be represented as the ratio between the partial pressures of water in a sample and pure water.

The pH may be expressed as follows:[27]

$$\mathrm{pH} = -\log(\gamma^*_{c_{H^+}} c_{H^+}) \tag{20}$$

where $\gamma^*_{c_{H^+}}$ is the activity coefficient for the asymmetric convention in a molar concentration scale. It is calculated from the asymmetric activity coefficient in a mole fraction scale according to the following equation:

$$\gamma^*_{c_{H^+}} = \frac{x_{H^+}}{c_{H^+} v_w^{oL}} \gamma^*_{H^+} \tag{21}$$

Water activities and pH were estimated by eqs 19 and 20, respectively, using the true species concentrations and their activity coefficients. Ideal pH values (no activity coefficient correction for all species in solution) were also computed as follows:

$$\mathrm{pH} = -\log(c_{H^+}) \tag{22}$$

Figures 1 and 2 compare respectively measured water activities and pH with those predicted by the UNIFAC model for binary systems at 298.15 K. Experimental and calculated water activities and pH for ternary systems are presented in Figures 3 and 4, respectively. The last one also shows ideal pH values. It can be seen that there is very good agreement between measured data and those predicted with the modified UNIFAC model, even at high solution concentration, showing that the calculated activity coefficients were able to represent satisfactorily the nonideality of the systems.

Average absolute deviations (AADs) per system and per property studied are presented in Table 8. AAD values for

Table 7. UNIFAC Group Interaction Parameters (*K*) for Polycarboxylic Acid Systems

	COOH	CH_2	CH	C	OH	COO^-	OH^-	H^+	H_2O
COOH		315.3	315.3	315.3	−4.179[b]	−2500.0	−2500.0	−2500.0	−71.53[b]
CH_2	663.5				986.5	−2500.0	0.0	−1150.0	1318.0
CH	663.5				986.5	−2500.0	0.0	−1150.0	1318.0
C	663.5				986.5	−2500.0	0.0	−1150.0	1318.0
OH	260.2[b]	156.4	156.4	156.4		−2500.0	−3450.0	−1650.0	353.50
COO^-	*a*	−746.3	−746.3	−746.3	497.3		0.0	−2500.0	700.0
OH^-	*a*	1753.7	1753.7	1753.7	452.7	0.0		−2500.0	−602.5
H^+	*a*	603.7	603.7	603.7	1347.3	−2500.0	−2500.0		843.8
H_2O	−324.7[b]	300.0	300.0	300.0	−229.1	−2500.0	−3802.5	−2356.2	

[a] Not yet available and set to zero. [b] Readjusted by Velezmoro.[31]

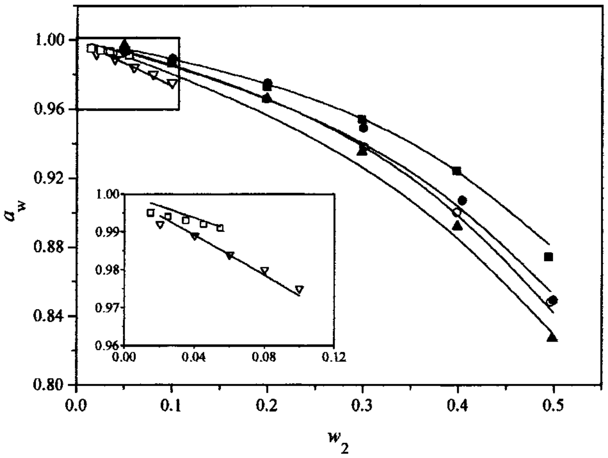

Figure 1. Experimental ((■) citric, (○) malic, (▲) malonic, (▽) oxalic, (□) succinic, and (●) tartaric acids) and predicted (—) water activities at 298.15 K.

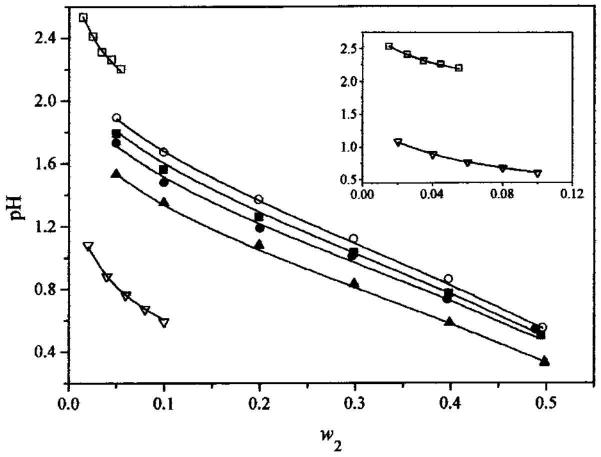

Figure 2. Experimental ((■) citric, (○) malic, (▲) malonic, (▽) oxalic, (□) succinic, and (●) tartaric acids) and predicted (—) pH at 298.15 K.

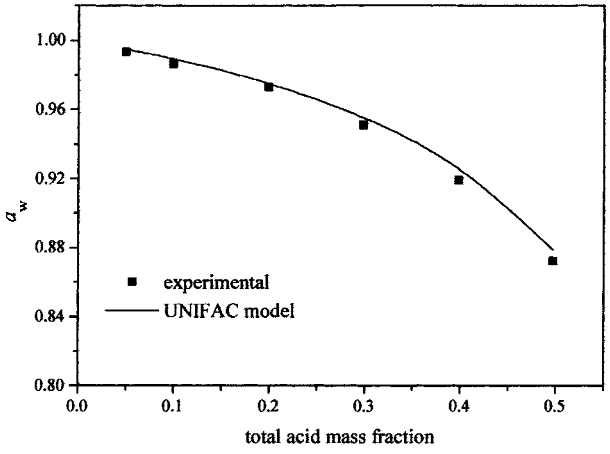

Figure 3. Experimental and predicted water activities for aqueous malic acid + citric acid mixtures at 298.15 K.

water activity were calculated according to the following equation:

$$\mathrm{AAD} = \left[\left(\sum_{n} \frac{|a^{\mathrm{exp}}_{\mathrm{w},n} - a^{\mathrm{cal}}_{\mathrm{w},n}|}{a^{\mathrm{exp}}_{\mathrm{w},n}}\right)\right] \times \frac{100}{n} \qquad (23)$$

where $a^{\mathrm{exp}}_{\mathrm{w},n}$ and $a^{\mathrm{cal}}_{\mathrm{w},n}$ are the experimental and calculated water activities, respectively, and n is the number of experimental points. Average absolute deviations for pH were also computed according to eq 23, substituting $a^{\mathrm{exp}}_{\mathrm{w},n}$ and $a^{\mathrm{cal}}_{\mathrm{w},n}$ by the experimental ($\mathrm{pH}^{\mathrm{exp}}_{n}$) and calculated ($\mathrm{pH}^{\mathrm{cal}}_{n}$) pH values, respectively.

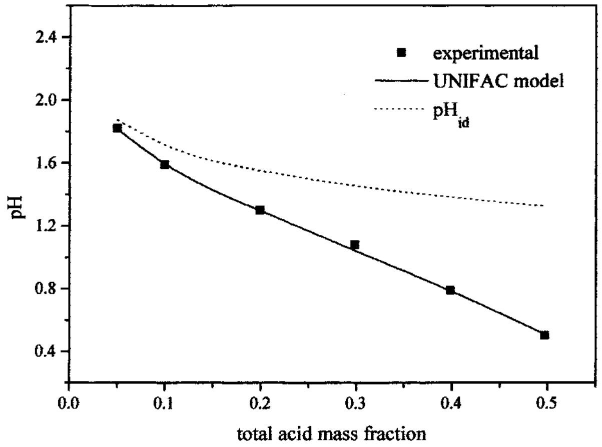

Figure 4. Experimental and predicted pH for aqueous malic acid + citric acid mixtures at 298.15 K.

Table 8. Water Activity and pH Prediction for Aqueous Polycarboxylic Acid Systems

	AAD/%		
aqueous system	a_{w}	pH	$\mathrm{pH}_{\mathrm{id}}$[a]
citric acid	0.34	1.01	52.96
malic acid	0.38	1.39	48.53
malonic acid	0.62	1.47	61.55
oxalic acid	0.11	0.93	3.46
succinic acid	0.15	0.44	2.08
tartaric acid	0.62	2.85	43.98
malic acid + citric acid	0.42	1.08	50.74
global	0.38	1.31	37.61

[a] Ideal pH.

As already expected, ideal pH values differed widely from experimental data in aqueous systems with high solute concentration, since they display a highly nonideal behavior. For more dilute (oxalic and succinic acid) systems, the AAD values obtained from ideal and measured pH values were lower.

As can also be seen from Table 8, AAD values between experimental data and those predicted by the modified UNIFAC model varied from 0.11% to 0.62% for water activity, and from 0.44% to 2.85% for pH, which clearly shows the high predictive performance of the selected model.

As already mentioned, an attempt to estimate nonavailable parameters did not affect significantly the predictive capacity of the model. Apparently, the previously readjusted parameters between the polar groups[31] are accurate enough to allow a very satisfactory description of water activity and pH by the modified UNIFAC model, so that an additional parameter adjustment does not have an impact on the quality of the prediction for the mixtures focused on in this work.

Conclusions

Water activities and pH for binary and ternary polycarboxylic acid systems were measured at 298.15 K. Experimental data were compared with those predicted by a modified UNIFAC group contribution model. In the model formulation, a Pitzer–Debye–Hückel term was added to represent the electrostatic interactions between ionic species. The solvation phenomenon between water and ions was also considered. To take into account all the ionic species which arose from the partial dissociation of weak acids, a numerical procedure based on chemical equilibrium constants, the electroneutrality condition, and stoichiometric balances was associated with the modified UNIFAC model.

The close agreement between measured and calculated data showed that the selected model can be successfully used for estimating physicochemical properties of mixtures with weak electrolytes. Its applicability for other partially dissociated aqueous systems important in the food industry should be considered in future work. This approach to water activity and pH prediction could be easily extended in calculation of various thermodynamic properties such as osmotic coefficient, boiling temperature, and freezing point.

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