UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ENGENHARIA DE ALIMENTOS
DEPARTAMENTO DE ENGENHARIA DE ALIMENTOS

DETERMINAÇÃO EXPERIMENTAL E MODELAGEM DE TEMPERATURA DE EBULIÇÃO E pH DE SISTEMAS BINÁRIOS CONTENDO COMPOSTOS PRESENTES EM SUCOS DE FRUTAS

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"Não é o muito saber que sacia e satisfaz, mas o sentir e saborear as coisas internamente"

Santo Inácio de Loyola

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DISSERTAÇÃO DE MESTRADO

AUTOR: Guilherme José Maximo

TÍTULO: Determinação experimental e modelagem de temperatura de ebulição e pH de sistemas binários contendo compostos presentes em sucos de frutas

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RESUMO

O equilíbrio líquido-vapor de soluções aquosas binárias formadas por açúcares presentes em sucos de fruta, D-glucose e D-frutose foi estudado através da determinação experimental da temperatura de ebulição em rotaevaporador com recirculação da fase vapor, de 20 kPa até a pressão atmosférica (93.6 kPa) e concentração entre 10 e 60 % (m/m). Os dados experimentais foram correlacionados com dados preditos a partir do cálculo do coeficiente de atividade pelo método de contribuição de grupos UNIFAC-Lyngby utilizando diferentes modelos moleculares e parâmetros estruturais. A conformação cíclica das moléculas foi decisiva na obtenção de resultados mais precisos pela modelagem. Os resultados foram descritos com precisão através de diagramas de *Dühring* e o aumento da temperatura de ebulição das soluções em relação à da água pura foi considerado significativo na demanda de energia para mudança de fase. O equilíbrio termodinâmico de soluções aquosas de ácidos policarboxílicos presentes em sucos e polpas de fruta, ácido cítrico, málico, malônico, oxálico, succínico e tartárico foram estudados através da determinação experimental do pH em células isotérmicas, entre 278.15 e 323.15 K e porcentagem mássica entre 1 e 20 %. Os dados experimentais foram correlacionados com dados preditos a partir da resolução de um sistema de equações não lineares em algorítmo computacional programado em MATLAB. O coeficiente de atividade foi calculado através da utilização isolada ou combinada, do método UNIFAC-Lyngby e da equação modificada de Debye-Hückel, levando em consideração as interações de curto e longo-alcance presentes na solução. De modo geral, o modelo combinado descreveu com melhor precisão o comportamento do pH das soluções do que a utilização dos modelos isolados. Além disso, de acordo com o equilíbrio químico das soluções, a temperatura tem efeito significativo no pH das soluções, o que significa que algumas propriedades dessas misturas são alteradas durante os processos térmicos.

Palavras-chave: UNIFAC, Temperatura de ebulição, pH, Açúcares, Ácidos policarboxílicos.

AUTHOR: Guilherme José Maximo

TITLE: Experimental determination and modeling of boiling point and pH of binary systems containing fruit juice compounds

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ABSTRACT

The vapor-liquid equilibrium of binary aqueous solutions of D-glucose and D-fructose, present in fruit juices, was evaluated by experimental boiling point measurements in a rotary evaporator with total reflux of the vapor phase from 20 kPa to atmospheric pressure (93.6 kPa) and concentration from 10 to 60 % by mass. The experimental data were correlated with predicted data by UNIFAC-Lyngby group contribution method, using different molecular approaches and structural parameters. The cyclic conformation of the sugar molecules was decisive for the accuracy of the modeling. The data were accurately described by Dühring diagrams and the rise in boiling point was considered significant for energy demand of phase change. The thermodynamic equilibrium of aqueous solutions of polycarboxylic acids present in fruit juices and pulps, citric acid, malic acid, malonic acid, oxalic acid, succinic acid and tartaric acid was evaluated by experimental pH measures in isothermic cells, from 278.15 to 323.15 K and concentration from 1 to 20 % by mass. The experimental data were correlated with predicted data by the resolution of a non-linear equation system by a computer algorithm implemented in MATLAB. The activity coefficients were calculated using the UNIFAC-Lyngby method and the modified Debye-Hückel term, taking into account the short and long-range interactions of the molecules in solution. In general, the combined model described the behavior of the pH of the solutions with higher accuracy than the isolated models. Moreover, according to chemical equilibrium of the solutions, the effect of temperature on pH was significant, meaning that some mixtures properties are affected during thermal processes.

Keywords: UNIFAC, Boiling point, pH, Sugar, Polycarboxylic acid

INTRODUÇÃO

Grande parte das exportações de produtos derivados do setor hortifrutícola no Brasil está relacionada aos sucos concentrados de fruta (INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA, 2008; INSTITUTO BRASILEIRO DE FRUTAS, 2008). Estes números demandam estudos sistemáticos sobre suas propriedades físico-químicas. Equipamentos otimizados e processos de transferência térmica e mássica mais eficientes são desenvolvidos através do conhecimento de propriedades como pH e temperatura de ebulição em função de parâmetros do processo e do produto. Dentre os constituintes dos sucos de fruta, os açúcares e ácidos policarboxílicos recebem atenção especial por serem seus compostos majoritários e determinarem, portanto, maior impacto em suas principais propriedades.

Em geral, sucos e polpas são concentrados por evaporação, conduzida à temperatura de ebulição do produto. A determinação desta propriedade é realizada através da avaliação do equilíbrio termodinâmico das fases deste sistema. O modelo UNIFAC (UNIversal Functional-group Activity Coefficient) (LARSEN; RASMUSSEN; FREDENSLUND, 1987) é um método preditivo utilizado para o cálculo do coeficiente de atividade de misturas binárias e multicomponentes e está baseado no conceito de contribuição de grupos. Através do coeficiente de atividade é possível determinar, teoricamente, a temperatura de ebulição em função da pressão e da composição de uma mistura. Sucos e polpas também apresentam em sua composição alguns eletrólitos, cujas espécies iônicas influenciam no desvio da idealidade de uma solução. Neste caso, é necessária a utilização de um modelo combinado que considere as interações de *curto e longo-alcance* entre os grupos presentes na mistura. Deste modo, o coeficiente de atividade pode ser calculado pela contribuição do método UNIFAC e da teoria de Debye-Hückel (PITZER, 1980) para sistemas de eletrólitos.

A avaliação do equilíbrio termodinâmico dos eletrólitos presentes em uma mistura permite a determinação teórica do pH em função de sua temperatura e composição. A partir desta propriedade, as características microbiológicas, enzimáticas e sensoriais de sistemas alimentícios podem ser mensuradas para o planejamento de uma operação unitária.

A determinação experimental da temperatura de ebulição e do pH de sucos e polpas de fruta, de soluções binárias e multicomponentes de açúcares e ácidos policarboxílicos, tem sido realizada extensamente pela literatura. Contudo, a modelagem destas propriedades continua sendo aprimorada através da determinação de parâmetros dos modelos, da utilização dos parâmetros existentes em sistemas diversos e do estudo dos efeitos da temperatura, da pressão e da composição dos sistemas na robustez dos modelos preditivos para o cálculo do coeficiente de atividade e para a predição das propriedades termodinâmicas. Deste modo, os processos podem ser otimizados com menores custos, menores tempos e maior eficiência.

Este trabalho está dividido em 3 capítulos. O primeiro pretende revisar os conceitos e os trabalhos publicados pela literatura referentes à determinação experimental e à modelagem de soluções aquosas alimentícias. O segundo e o terceiro capítulo pretendem ampliar a discussão e apresentar a metodologia aplicada, medidas experimentais, avaliação preditiva e a discussão dos resultados obtidos. Dentre esses capítulos, o primeiro propõe a determinação experimental e a modelagem das propriedades de equilíbrio e da temperatura de ebulição de soluções de açúcares e o segundo propõe a avaliação do equilíbrio termodinâmico e do pH de soluções de ácidos policarboxílicos. Estes capítulos foram redigidos no formato de artigo científico com o objetivo de serem publicados em revistas da área.

OBJETIVOS

Embora algumas extensões do equilíbrio líquido-vapor de soluções aquosas de açúcares e do equilíbrio líquido-líquido de soluções aquosas de ácidos policarboxílicos tenham sido estudadas pela literatura, este trabalho pretendeu ampliar a discussão relacionada aos atuais modelos para predição do coeficiente de atividade destas soluções e contribuir com a geração de dados experimentais que integrem o banco de dados da literatura da área, com relação às propriedades (temperatura de ebulição e pH) e aos processos particulares da engenharia de alimentos, com destaque à indústria de sucos e polpas de fruta, de forma a serem utilizados por outros pesquisadores. Em particular, os objetivos deste trabalho foram:

i) Avaliar o efeito das baixas pressões e altas concentrações na determinação experimental do equilíbrio líquido-vapor de soluções aquosas de monossacarídeos presentes em sucos concentrados de fruta (D-glucose e D-frutose) e correlacionar os dados com o seu comportamento termodinâmico a partir da construção de diagramas que relacionem o aumento da temperatura de ebulição destas soluções com a temperatura de ebulição da água pura, de modo a serem utilizados no dimensionamento de equipamentos e processos.

ii) Comparar alguns métodos na decomposição dos grupos moleculares presentes em soluções aquosas de açúcares utilizados pela literatura atual para a predição do coeficiente de atividade a partir do método UNIFAC-Lingby e correlacioná-los com os dados experimentais obtidos para temperatura de ebulição.

iii) Avaliar o efeito da temperatura no pH de soluções aquosas de ácidos policarboxílicos diluídas e com concentrações moderadas (concentrações observadas em sucos e polpas concentradas de fruta e *in natura*) e correlacionar os dados com o equilíbrio químico das soluções.

iv) Avaliar o comportamento do método UNIFAC-Lyngby e da equação modificada de Debye-Hückel proposta por Pitzer (1980) na predição do coeficiente de atividade das soluções aquosas de ácidos policarboxílicos e correlacionar os dados a partir das interações moleculares existentes em soluções não-diluídas de eletrólitos.

v) Aprimorar a predição das propriedades de equilíbrio a partir da construção de um algoritmo implementado em MATLAB para a resolução numérica dos sistemas de equações não-lineares para a determinação do equilíbrio de fases das soluções avaliadas através da utilização de variáveis independentes que produzam resultados mais precisos.

CAPÍTULO 1

Revisão Bibliográfica

REVISÃO BIBLIOGRÁFICA

1.1 Sucos de fruta e seus constituintes: açúcares e ácidos policarboxílicos

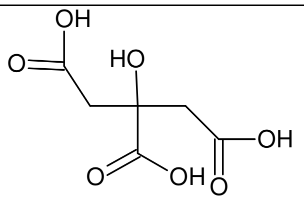
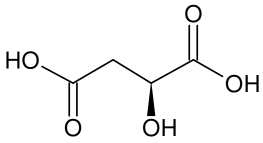
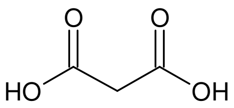
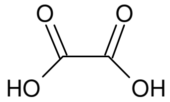
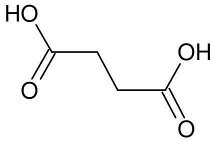
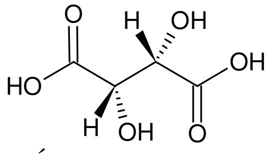
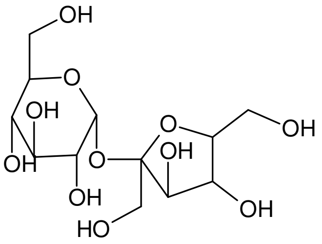
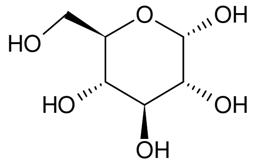
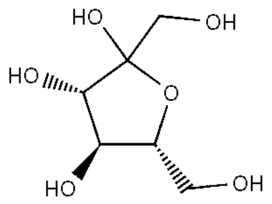
Sucos de fruta são misturas aquosas compostas por açúcares, ácidos policarboxílicos, ácidos graxos, sais, pectina, voláteis aromatizantes, pigmentos, proteínas e vitaminas (BOBBIO; BOBBIO, 1992). Os ácidos orgânicos e os açúcares são suas principais substâncias solúveis. Entre os ácidos policarboxílicos destacam-se o ácido málico (presente em polpas de maçã, pêssego, cereja e no hipocótilo de girassol), o ácido cítrico (presente em sucos de limão, laranja, grapefruit, abacaxi e tangerina, em folhas de capim elefante e cana-de-açúcar), o ácido oxálico (presente na folha de espinafre e em polpas de abacaxi e morango), os ácidos malônico e succínico (presentes na cevada e no caldo de cana-de-açúcar) e o ácido tartárico (presente no suco de uva) (GUTIERREZ; FERRARI; ORELI, 1989; CHEN, 1993; MEDEIROS, 2001; BUENO et al., 2002; RIGHETTO, 2003; MEDEIROS et al., 2005; BARATO, 2008; NÚCLEO DE ESTUDOS E PESQUISAS EM ALIMENTAÇÃO, 2008). Entre os açúcares destacam-se a sacarose, ou α-D-glucopiranosil-β-D-frutofuranosídeo, um dissacarídeo não-redutor formado por uma unidade de D-glucopiranose e outra de D-frutofuranose, e os monossacarídeos redutores, D-frutose e D-glucose. A sacarose ocorre em maior quantidade na cana-de-açúcar e na beterraba. A D-glucose e a D-frutose ocorrem em frutas e mel, em suas formas livres, e participam da formação de outros polissacarídeos encontrados em espécies vegetais, tais como a amilose e a celulose (polissacarídeos lineares, formados por 1 unidade de D-glucopiranose), a D-maltose (dissacarídeo redutor, constituído por 2 unidades de D-glucopiranose) e a lactose (dissacarídeo constituído por 1 unidade de D-glucopiranose e outra de D-galactopiranose) (BOBBIO; BOBBIO, 1992). A Tabela 1.1 apresenta os valores relativos à composição média de alguns sucos e polpas de frutas não-concentrados e a Tabela 1.2 apresenta as estruturas químicas dos principais ácidos orgânicos e açúcares encontrados em sucos de frutas e espécies vegetais, obtidas a partir do banco de dados do National Bureau of Standards (2009)

Tabela 1.1 - Composição média de sucos e polpas não-concentrados de algumas frutas (g de composto / 100 g de polpa)

Polpa	*Ref.*	*Açúcares*	*Frutose*	*Glicose*	*Sacarose*	*Ácido cítrico*	*Ácido málico*	*Gordura*	*Fibras*	*Proteínas*	*Cinzas*
Abacate	[1]	8,14	-	-	-	-	-	3,25	3,00	1,20	0,50
Abacaxi	[2]	13,00	2,1-2,4	2,1-2,4	8,4-9,5	0,7-0,9	0,1-0,2	0,10	1,00	0,50	0,40
Açaí	[3]	6,60	-	-	-	-	-	5,30	-	0,11	0,26
Acerola	[4]	7,14	8,8 *		-	1,40	-	0,32	0,55	0,68	0,45
Banana	[5]	24,43	-	-	-	-	-	0,08	0,81	1,96	0,40
Cajá	[2]	5,90	8,0 *		-	1,40	-	1,26	0,25	1,30	0,40
Caju	[6]	8,34	7,7-8,9 *		0,2-0,5	-	0,2-0,8	0,25	0,80	0,68	0,37
Cupuaçu	[1]	11,40	4,7 *		-	1,90	-	0,60	1,60	0,80	0,60
Graviola	[1]	9,80	-	-	-	-	-	0,10	1,20	0,60	0,40
Laranja	[2]	8,60	1,6-3,0	1,0-2,6	3,1-5,1	0,4-1,5	0,1-0,3	0,10	0,40	1,10	0,30
Limão	[2]	7,30	-	-	-	-	-	0,10	-	0,60	0,30
Maçã	[1]	12,50	3,0-10,5	1,8-4,1	0,5-5,6	0,01-0,04	0,2-1,3	-	1,50	0,20	0,30
Manga	[1]	12,50	6,0 *		-	1,0	-	0,20	1,10	0,40	0,40
Maracujá	[7]	9,60	-	-	-	-	-	0,20	0,45	0,80	0,50
Pinha	[8]	22,48	-	-	-	-	-	0,72	3,50	1,50	0,70
Serigüela	[1]	10,76	10,0 *		-	1,2	-	0,31	0,64	-	-
Tangerina	[2]	8,80	-	-	-	-	-	-	-	0,50	0,30
Tomate	[1]	6,90	-	-	-	-	-	-	1,00	1,40	1,00
Umbu	[8]	8,80	5,7 *		-	1,7	-	0,10	1,30	0,50	0,40
Uva	[2]	16,80	8,0	7,8	0,2-2,3	0,02-0,05	0,3-0,7	-	0,20	0,20	0,20

Ref.:[1] NÚCLEO DE ESTUDOS E PESQUISAS EM ALIMENTAÇÃO, 2008; [2] Bueno et al., 2002; [3] Nascimento et al., 2008; [4] Righetto, 2003; [5] Medeiros et al, 2005; [6] Barato, 2008; [7] Gratão, Silveira Junior e Polizelli, 2005; [8] Medeiros, 2001;* g de frutose + glicose / 100 g de polpa.

Tabela 1.2 - Estrutura química de ácidos policarboxílicos e açúcares presentes em sucos de frutas (NATIONAL BUREAU OF STANDARDS, 2009)

Fórmula estrutural			
Composto	Ácido Cítrico MM= 192.1235 g. gmol^{-1}	Ácido L-Málico MM = 134.0874 g. gmol^{-1}	Ácido Malônico MM = 104.0615 g. gmol^{-1}
Fórmula estrutural			
Composto	Ácido Oxálico MM = 90.0349 g. gmol^{-1}	Ácido Succínico MM = 118.0880 g. gmol^{-1}	Ácido D-Tartárico MM = 150.0868 g. gmol^{-1}
Fórmula estrutural			
Composto	Sacarose MM = 342.2965 g.gmol^{-1}	β-D-Glucose MM = 180.1559 g.gmol^{-1}	β-D-Frutose MM = 180.1559 g.gmol^{-1}

Os ácidos policarboxílicos são especialmente responsáveis pela acidez dos sucos e polpas de fruta e utilizados, pela indústria de alimentos, como acidificantes e anti-oxidantes. A concentração de ácidos orgânicos nestes sistemas é dependente do grau de maturação, varia entre 0,3 e 3,1 % (m/m) da composição e determina valores de pH entre 2,0 (lima e limão) e 4,5 (tomates e uvas), aproximadamente (RAMASWAMY, 2005; WEAST, 1981). Em solução aquosa, ácidos dicarboxílicos (ácidos málico, malônico, oxálico, succínico e tartárico) e tricarboxílicos (ácido cítrico) dissociam-se, produzindo espécies iônicas e moleculares. A literatura reporta que esta dissociação é dependente da temperatura (LEVINE, 2002, ATKINS; DE PAULA, 2002), de modo que o pH dos sistemas alimentícios pode variar durante os processos térmicos. A acidez de sucos e polpas de fruta permite a utilização de tratamentos térmicos menos rigorosos e contribui na sua caracterização sensorial, físico-química e microbiológica. (RAMASWAMY, 2005).

Os açúcares redutores, D-glucose e a D-frutose, de acordo com Shallenberger e co-autores (1977) e Maple e Allerhand (1987), apresentam 4 formas isoméricas em solução aquosa, cujas concentrações são dependentes da temperatura e cujas estruturas possuem propriedades específicas: α e β-D-frutofuranose, α e β-D-frutopiranose, α e β-D-glucofuranose e α e β-D-glucopiranose. Quando estes açúcares são aquecidos em soluções ácidas (como é o caso dos sucos de frutas) ou básicas, sofrem desidratação e formam, entre outros compostos, o hidroximetilfurfural (HMF), composto responsável pelo aroma e cor característico do processo denominado caramelização. Nestas condições, a sacarose pode ser hidrolisada em D-frutofuranose e D-glucopiranose. Esta reação é conhecida como inversão da sacarose (devido a inversão da rotação ótica da solução inicial) e o produto final da hidrólise é conhecido como açúcar invertido. Os açúcares redutores (D-glucose ou D-frutose), por outro lado, na presença de amino-ácidos, catalisados ou não pela temperatura ou pela presença de ácidos, formam, após degradação, compostos voláteis e não voláteis responsáveis pelo escurecimento e o aroma característicos do processo denominado *Reação de Maillard* (BOBBIO; BOBBIO, 1992). Por este motivo, processos térmicos relacionados a sistemas alimentícios apresentam problemas particulares que devem ser levados em consideração durante o seu planejamento.

1.2 Transferência de calor e massa e o equilíbrio líquido-vapor

> *“ O levantamento ebulioscópico é a diferença entre a temperatura de ebulição de uma solução e a temperatura de ebulição da água (solvente) na mesma pressão. (...) Quando o levantamento ebulioscópico é diminuído da diferença aparente de temperatura, chega-se à diferença de temperatura corrigida do levantamento ebulioscópico e ao coeficiente de transferência de calor corrigido do levantamento ebulioscópico. São estes os parâmetros mais comuns para exprimir os dados de transferência de calor nos evaporadores. (...) Constituem também a melhor base para comparar o desempenho de vários tipos de evaporadores”* (PERRY; CHILTON, 1986)

Através desta observação, Perry e Chilton (1986) apontam para a importância do estudo das propriedades termodinâmicas no projeto de equipamentos industriais. Dentre os parâmetros envolvidos nos processos de transferência de calor e massa, a temperatura de ebulição é uma propriedade capaz de afetar as taxas de transferência do processo (Eq. 1.1) (FOUST et al., 1982; HELDMAN; SINGH, 1981).

$$Q = UA\,(T_v - T_p) \tag{1.1}$$

onde Q é a taxa de transferência de energia do processo, U é o coeficiente global de transferência de calor do equipamento, A é a área de transferência térmica e T_p e T_v são as temperaturas do produto e do vapor de aquecimento. A diferença entre a temperatura do vapor utilizado para a troca térmica e a temperatura de ebulição do produto determina a força motriz do processo de transferência de calor. Quando não se dispõe dos dados de entalpia ou de calores específicos da solução, é possível estimar o calor necessário através da soma do calor sensível, necessário para aquecer a alimentação até a temperatura final do produto, com o calor para a evaporação da água (PERRY; CHILTON, 1986). Contudo, sendo a temperatura de ebulição uma propriedade dependente da composição, a solução entrará em ebulição a uma temperatura mais alta que a temperatura da água pura, na mesma pressão. Se a elevação da temperatura de ebulição do produto em relação à da água for desconsiderada em um processo de evaporação, a força motriz será insuficiente para a evaporação do produto e a área de troca térmica do evaporador será subdimensionada (VARSHNEY; BARHATE, 1978). Este fato pode ser observado nas Figuras 1.1 e 1.2, que apresentam a dependência do coeficiente global de transferência de calor em evaporadores verticais de tubo longo e tubo curto em relação à temperatura de ebulição da mistura.

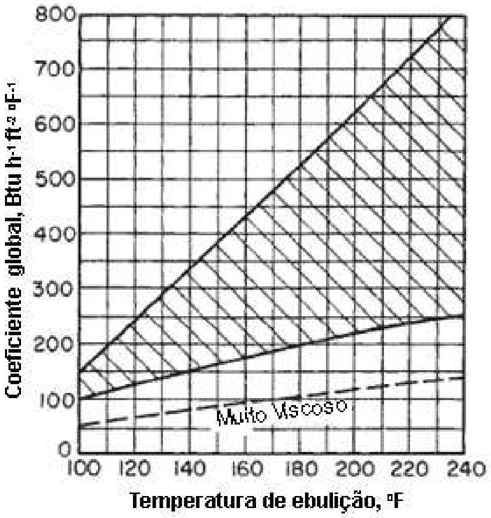


Figura 1.1 Faixa geral dos coeficientes globais em evaporadores verticais de tubo longo. (PERRY; CHILTON, 1986)

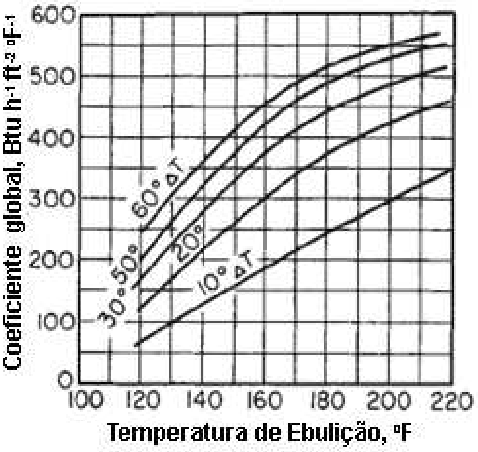


Figura 1.2 Coeficientes globais de transferência de calor em evaporadores de tubo curto. (PERRY; CHILTON, 1986)

Para a avaliação do comportamento da temperatura de ebulição de sistemas binários ou multicomponentes, em geral, são construídos diagramas experimentais que relacionam a temperatura de ebulição da solução e a temperatura de ebulição do solvente desta solução. *Dühring*, em 1878, observou que este comportamento era linear, concluindo que a pressão exerce pouca influência no aumento da temperatura de ebulição, exceto para sistemas extremamente não-ideais (FOUST et al., 1982). Inúmeros autores têm avaliado o aumento da temperatura de ebulição de sucos de frutas e de soluções de açúcares. Varshney e Barhate (1978) publicaram estudos ebuliométricos de sucos concentrados de abacaxi, manga e limão e publicaram diagramas de *Dühring* referentes a esses sistemas. Moresi e Spinosi (1984b) e Crapiste e Lozano (1988) avaliaram o efeito da pressão e da concentração na elevação da temperatura de ebulição de sucos de maçã, Moresi e Spinosi (1980, 1984a) de sucos de laranja e uva e Ilangantileke, Ruba e Joglekar (1992) de sucos de tangerina. Abderafi e Bounahmidi (1994, 1999) estudaram o equilíbrio líquido-vapor de sucos industriais de cana e beterraba e soluções binárias e multicomponentes de açúcares, aminoácidos e ácidos policarboxílicos. Telis-Romero e co-autores (2002, 2007) representaram a elevação do ponto de ebulição de suco de *grapefruit* e extrato de café em diagramas de *Dühring* e Gabas e co-autores (2008) publicaram dados similares utilizando sucos de amora. As Figuras 1.3 e 1.4 apresentam diagramas de *Dühring* retirados da literatura.

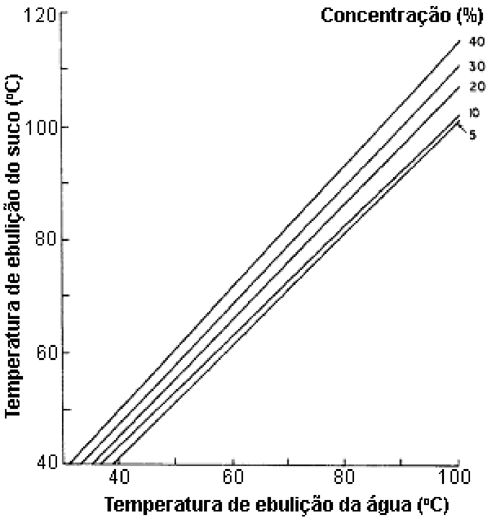


Figura 1.3 Diagrama de Dühring para suco de manga (VARSHNEY; BARHATE, 1978)

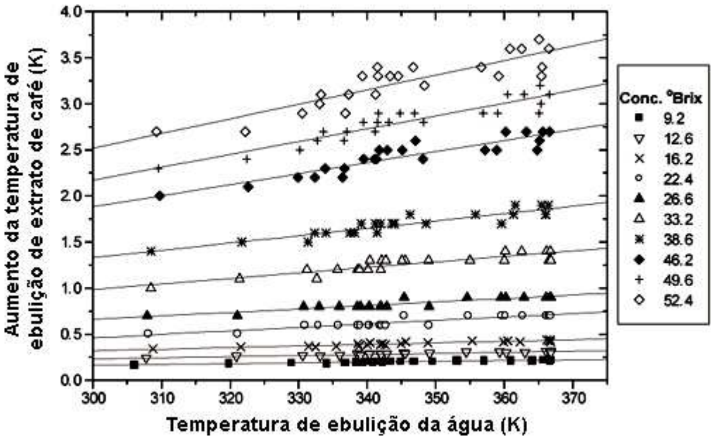


Figura 1.4 Aumento da temperatura de ebulição de extrato de café em diferentes concentrações de sólidos solúveis como função do ponto de ebulição da água pura (TELIS-ROMERO et al., 2002).

Os dados obtidos por estes diagramas são utilizados na elaboração de cartas que descrevem o comportamento das taxas de transferência térmica e da eficiência energética de equipamentos que dependem da temperatura de ebulição da solução como os evaporadores e os condensadores. As Figuras 1.5 e 1.6 apresentam nomogramas industriais construídos a partir de dados obtidos por levantamento ebuliométrico e diagramas de *Dühring* de soluções aquosas.

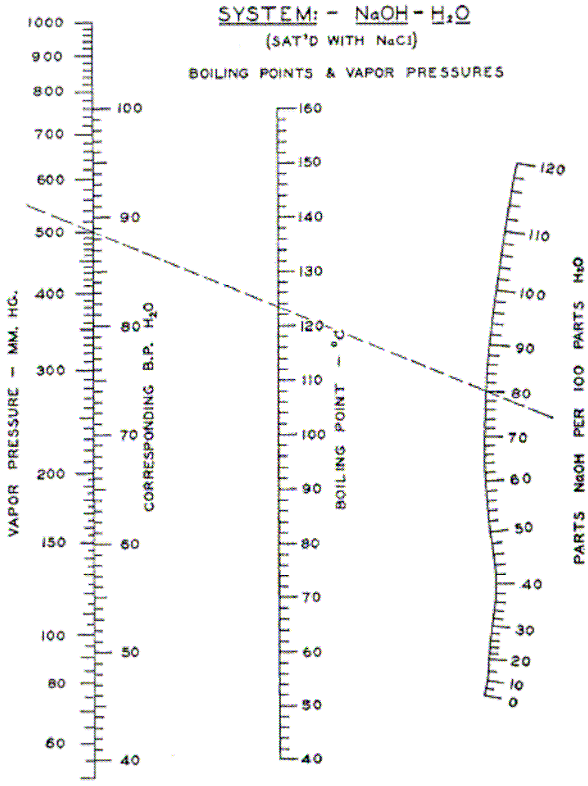


Figura 1.5 Nomograma industrial construído a partir de dados obtidos por Diagrama de Dühring para soluções de NaOH + água (RAVENSCROFT, 1929)

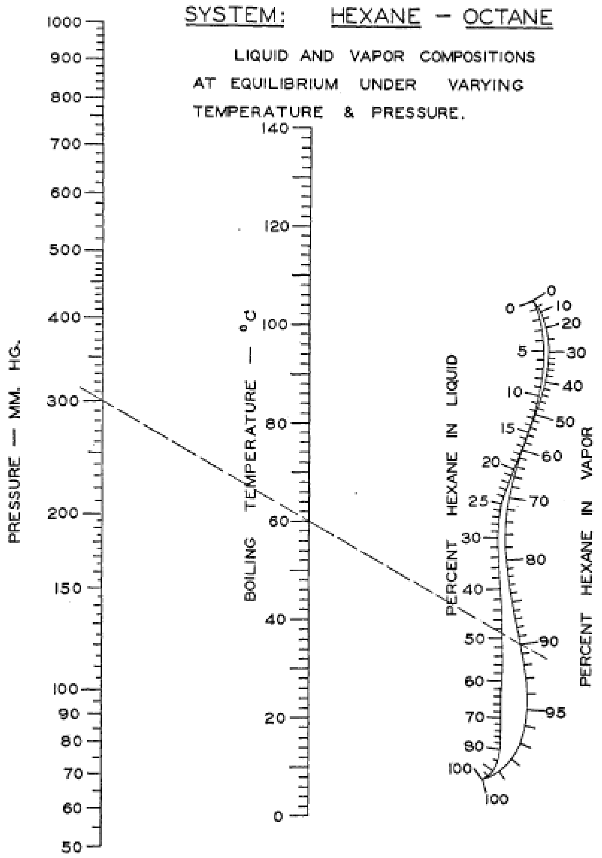


Figura 1.6 Nomograma industrial construído a partir de dados ebuliométricos de soluções de Hexano + octano (RAVENSCROFT, 1929)

Sucos de frutas são concentrados entre 10 e 70 ºBrix (SERVIÇO BRASILEIRO DE RESPOSTAS TÉCNICAS, 2007). Devido à sua termosensibilidade, o projeto de evaporadores deve estar baseado nas modificações estruturais, bioquímicas, sensoriais e termobacteriológicas particulares destes sistemas quando submetidos ao processamento (McLELLAN; PADILLA-ZAKOUR, 2005). Para evitar o processo de termodegradação são necessárias, portanto, menores temperaturas ou tempos de residência, através da diminuição do volume de alimentação ou da pressão do sistema (GLOVER, 2004).

Processos de evaporação estão baseados no equilíbrio líquido-vapor (ELV) do sistema. O ELV de uma solução é determinado quando as fugacidades de cada componente nas duas fases em equilíbrio se igualam, de acordo com a equação 1.2 (REID; PRAUSNITZ; POULING, 1987; LEVINE, 2002)

$$f_i^L(T,P,x_i) = f_i^V(T,P,y_i) \tag{1.2}$$

onde f_i representa a fugacidade do composto *i,* o sobrescrito *L* e *V* as fases líquida e vapor, x e y_i as frações molares do composto *i* nas fases líquida e vapor, respectivamente, *T* e *P* a temperatura e pressão do sistema. Este critério estabelece a equação 1.3.

$$y_i P \phi_i = x_i P_i^{vap} \gamma_i \tag{1.3}$$

onde, P_i^{vap} é a pressão de vapor do composto *i* na temperatura avaliada, ϕ_i e γ_i representam os coeficientes de fugacidade e atividade do composto *i* nas fases vapor e líquida, respectivamente, dados pelas equações 1.4 e 1.5 (REID; PRAUSNITZ; POULING, 1987; LEVINE, 2002).

$$\phi_i = \frac{f_i^V(T,P,y)}{y_i P} \tag{1.4}$$

$$\gamma_i = \frac{f_i^L(T,P,x)}{x_i f_i^o} \tag{1.5}$$

onde f_i^o representa a fugacidade do composto *i* puro à temperatura e pressão avaliadas. Considerando a fase vapor como ideal (coeficiente de fugacidade aproximadamente igual a 1) e sabendo que em baixas pressões a fugacidade do composto *i* puro é aproximadamente igual à pressão de vapor deste composto na temperatura avaliada, o equilíbrio líquido-vapor de uma solução com *n* componentes, pode ser estabelecido pelo sistema de equações abaixo (Eq. 1.6).

$$\begin{cases} y_1P = x_1P_1^{vap}\gamma_1 \\ y_2P = x_2P_2^{vap}\gamma_2 \\ \ldots \\ y_nP = x_nP_n^{vap}\gamma_n \end{cases} \tag{1.6}$$

Para uma solução aquosa formada por um soluto não volátil, ou seja, a fração molar da água na fase vapor é igual à unidade (y_1 = 1,0), a pressão total do sistema pode ser, então, calculada através da relação $P = x_1P_1^{vap}\gamma_1.$, onde o subescrito *1* refere-se à água. Estabelecendo a pressão do processo, a temperatura de ebulição pode ser estimada por método iterativo de modo que a raiz da equação 1.7 seja estabelecida.

$$P - x_1P_1^{vap}\gamma_1 = 0 \tag{1.7}$$

Para este caso, a adição de solutos na solução diminuirá a fração molar de solvente, o potencial químico da fase vapor ($\mu_{água}^{V} = \mu_{água}^{L} + RT \ln x_{água}$), a fugacidade dos compostos e aumentará a entropia da fase condensada. Portanto, será necessária uma maior adição de energia para a mudança de fase do solvente. De fato, levando em consideração a *lei de Raoult* ($P_{água} = x_{água}\, P_{água}^{vap}$) tem-se que a pressão parcial da água diminui com a adição de solutos. Em conseqüência, a solução necessitará de uma maior temperatura para que a pressão parcial da água se iguale com a pressão externa e evapore. Portanto, espera-se que o aumento da concentração de solutos resulte em aumento da temperatura de ebulição da solução (VARSHNEY; BARHATE, 1978; ATKINS; DE PAULA, 1994).

1.3 Equilíbrio químico e pH

> *"Alguns sistemas alimentícios são misturas aquosas complexas que contém uma extensa variedade de componentes. Sucos de frutas, extrato de café e óleos vegetais são, provavelmente, bons exemplos de soluções alimentícias. São processadas por diversas técnicas, como evaporação, liofilização, secagem, cristalização e extração para tornarem-se apropriadas para o consumo humano, serem estocadas por um longo tempo ou facilitarem o preparo de outros produtos. (...) Estes produtos estão sujeitos a necessidades especiais, tais como pH, pressão osmótica e atividade de água"* (MEIRELLES et al., 2003)

Na revisão publicada por Meirelles e co-autores (2003), atenção especial é dada para o conhecimento preciso das propriedades físico-químicas e do equilíbrio termodinâmico no desenvolvimento e otimização dos processos da engenharia de alimentos. O pH é uma propriedade físico-química que influencia três fatores relacionados ao processamento de alimentos: microbiológico, enzimático e sensorial (BOBBIO; BOBBIO, 2001) e cuja diminuição permite o abrandamento do tempo e da temperatura de processos térmicos (BOBBIO; BOBBIO, 2001; CHEN, 1993). Esta propriedade pode ser estimada através da avaliação do equilíbrio estequiométrico da mistura e da dissociação dos eletrólitos presentes no sistema. Para a predição do pH de uma solução aquosa de um ácido dicarboxílico H_2X, por exemplo, é necessário o conhecimento das equações de equilíbrio químico (Eqs. 1.8 a 1.10), dos balanços de massa (Eqs. 1.11 e 1.12), da condição de eletroneutralidade (Eq. 1.13) e das constantes de dissociação dos eletrólitos (K_1 *e* K_2) para o cálculo das concentrações das espécies e dos coeficientes de atividade (Eqs. 1.14 e 1.15).

$$H_2X \leftrightarrow HX^- + H^+ \qquad K_1 \tag{1.8}$$

$$HX^- \leftrightarrow X^{--} + H^+ \qquad K_2 \tag{1.9}$$

$$H_2O \leftrightarrow OH^- + H^+ \qquad K_{água} \tag{1.10}$$

$$c_{H_2X,o} = c_{H_2X,f} + c_{HX^-} + c_{X^{--}} \tag{1.11}$$

$$c_{H_2O,o} = c_{H_2O,f} + c_{OH^-} \tag{1.12}$$

$$c_{H^+} = c_{OH^-} + c_{HX^-} + 2c_{X^{--}} \tag{1.13}$$

$$K_1 = \frac{(\gamma^*_{H^+} c_{H^+})(\gamma^*_{HX^-} c_{HX^-})}{(\gamma^*_{H_2X} c_{H_2X})} \tag{1.14}$$

$$K_2 = \frac{(\gamma^*_{H^+} c_{H^+})(\gamma^*_{X^{--}} c_{X^{--}})}{(\gamma^*_{HX^-} c_{HX^-})} \tag{1.15}$$

onde c_i é a concentração molar da espécie i (mol . L^{-1}) e γ^*_i , o coeficiente de atividade da espécie i na convenção assimétrica. A convenção assimétrica adota como estado padrão de cada componente i da solução, a solução infinitamente diluída de i à pressão da solução (ou seja, $\gamma_i \rightarrow 1$ quando $x_i \rightarrow 0$). Usando este grupo de equações e um modelo preditivo para o cálculo do coeficiente de atividade, as concentrações das espécies podem ser calculadas e o pH predito através da equação 1.16 (LEVINE, 1995; MEIRELLES et al, 2003)

$$pH = -\log(\gamma^*_{H^+}\ c_{H^+}) \tag{1.16}$$

onde c_{H+} e γ^*_{H+} se referem à concentração molar dos íons H^+, e ao coeficiente de atividade da espécie H^+, respectivamente. O princípio de Le Chatelier (ATKINS; DE PAULA, 2002) propõe que o equilíbrio químico da solução é alterado pela temperatura do sistema, de modo que, quando há aumento de temperatura, as reações exotérmicas favorecem os reagentes e reações endotérmicas favorecem os produtos. A alteração do equilíbrio químico sugere que o pH também varie em função da temperatura. De fato, termodinamicamente, o pH (ou, a atividade de uma espécie iônica) pode ser definido pela equação 1.17 (DURST; BATES, 1981). Esta equação concorda com a equação de van´t Hoff (ATKINS; DE PAULA, 2002) que apresenta a constante de dissociação *K* como função da temperatura (Eq. 1.18)

$$pH\,(X) = pH\,(S) - (\,E_X - E_S\,)\,F\,(2.303\,R\,T)^{-1} \tag{1.17}$$

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^{\theta}}{RT^2} \tag{1.18}$$

onde *X* se refere à amostra, *S* à solução referência, *E* é a força eletromotriz (emf) das soluções *X* e *S*, *F* e *R* são constantes universais dos gases, $\Delta_r H^{\theta}$ é a entalpia padrão da reação à temperatura *T*

A literatura apresenta trabalhos relativos ao estudo da variação do pH de sistemas químicos, alimentícios e não alimentícios através do ajuste do equilíbrio químico, salientando a sua extensão e aplicabilidade. Quoc, Lamarche e Maklouf (2000), por exemplo, avaliaram o efeito de parâmetros da eletrodiálise na alteração do pH de sucos não-clarificados de maçã com o objetivo de inibir a atividade da enzima polifenol-oxidase e estabilizar a cor do sistema. Cunningham (2009) cita diversos estudos relativos ao efeito do pH dos alimentos na acidez da urina, na manutenção do pH do soro, no desenvolvimento da osteoporose, e em processos de homeostase, através de avaliação experimental ou modelagem. Rosenthal (1948) conduziu um dos poucos estudos sobre o efeito da temperatura na alteração do pH em sistemas orgânicos com aplicação prática. Ele verificou que a variação da temperatura ambiente é significativa para a alteração do pH de plasma sanguíneo, afetando a análise de dados laboratoriais. Nordstrom et al. (2000) realizaram determinações experimentais e modelagem do pH de sistemas geológicos cuja contaminação por metais havia induzido à diminuição do pH destes sistemas para valores negativos e concluíram que modelos teóricos são ferramentas úteis para responder algumas questões relacionadas a esses cenários.

1.4 Métodos para a predição do coeficiente de atividade

> *"O desenvolvimento e o a aplicação das operações unitárias nas indústrias químicas e bioquímicas necessitam da compreensão de misturas complexas em cujos processos estão envolvidas. Do mesmo modo que as espécies variam quanto ao tamanho e o comportamento molecular, a água, os ácidos orgânicos, bases, eletrólitos, aminoácidos e metabólitos ocorrem simultaneamente em extratos celulares ou meios de fermentação e a modelagem dessas interações e do equilíbrio de fases se torna difícil"* (ACHARD; DUSSAP; GROS, 1994)

Achard, Dussap e Gros (1994), em sua publicação sobre a modelagem do equilíbrio de fases de misturas complexas, abordam a importância e a dificuldade da predição do comportamento não-ideal das soluções. A modelagem teórica das propriedades termodinâmicas de um sistema pode ser conduzida através de dois métodos comumente empregados para o cálculo do equilíbrio de fases, i) o método ϕ-ϕ , que calcula os coeficientes de fugacidade (ϕ) dos componentes da mistura, em ambas as fases, por intermédio de uma única equação de estado, como a equação de estado cúbica de Peng–Robinson e ii) o método γ-ϕ que emprega modelos distintos para o cálculo do coeficiente de atividade (γ) na fase líquida e o coeficiente de fugacidade (ϕ) na fase vapor (PEROZIN, 2003). O método de contribuição de grupos UNIFAC (FREDENSLUND; JONES; PRAUSNITZ, 1975) é um modelo para o cálculo de γ, extensamente utilizado como alternativa para a simulação de processos em misturas multicomponentes e está baseado no modelo molecular UNIQUAC (Universal QUAseChemical) (ABRAMS; PRAUSNITZ, 1975)**.** Considera que, a partir da análise do conjunto dos grupos funcionais presentes em um composto ou uma mistura, o coeficiente de atividade dos compostos de uma solução pode ser predito através do somatório de parâmetros relativos à contribuição destes grupos no desvio da idealidade da mistura. O cálculo de γ pelo método UNIFAC é dado pela soma de uma parte combinatorial (γ_i^c) e uma residual (γ_i^r) (Eq. 1.19)

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r \tag{1.19}$$

onde o termo combinatorial é função de parâmetros relativos ao tamanho e à forma dos grupos presentes na mistura e pode ser calculado a partir das equações 1.20 a 1.25

$$\ln \gamma_i^c = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\Theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{n} x_j l_j \tag{1.20}$$

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^{n} r_j x_j} \tag{1.21}$$

$$\Theta_i = \frac{q_i x_i}{\sum_{j=1}^{n} q_j x_j} \tag{1.22}$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \quad \text{, sendo z = 10} \tag{1.23}$$

$$r_i = \sum_{k=1}^{n} v_k^{(i)} R_k \tag{1.24}$$

$$q_i = \sum_{k=1}^{n} v_k^{(i)} Q_k \tag{1.25}$$

onde x_i é a fração molar do composto i, Φ_i é a fração volumétrica da molécula, Θ_i é a fração de superfície, r_i e q_i são parâmetros calculados a partir da somatória dos termos referentes ao volume R_k e à área de superfície Q_k dos grupos, apresentados em bancos de dados da literatura. O termo residual, função de parâmetros relativos às interações de energia entre os grupos é calculado através das equações 1.26 a 1.30.

$$\ln \gamma_i^r = \sum_{k=1}^{n} \nu_k^i \left[\ln \Gamma_k - \ln \Gamma_k^{(i)}\right] \tag{1.26}$$

$$\text{onde, } \ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_{m=1}^{n} \Psi_m \tau_{mk} \right) - \sum_{m=1}^{n} \frac{\Psi_m \tau_{mk}}{\sum_{p=1}^{n} \Psi_p \tau_{pm}} \right] \tag{1.27}$$

$$\Psi_m = \frac{Q_m X_m}{\sum_{p=1}^{n} Q_p X_p} \tag{1.28}$$

$$X_m = \frac{\sum_{j=1}^{n} \nu_m^{(j)} x_j}{\sum_{j=1}^{n} \sum_{p=1}^{n} \nu_p^{(j)} x_j} \tag{1.29}$$

$$\tau_{mn} = \exp\left(\frac{-a_{mn}}{T} \right) \tag{1.30}$$

onde, ν_k^i é o número de grupos do tipo *k* na molécula *i*; Γ_k é o coeficiente de atividade do grupo *k* na composição da mistura, $\Gamma_k^{(i)}$ é o coeficiente de atividade do grupo *k* numa composição de grupos correspondente a uma substância pura *i* , Ψ_i é a fração de área superficial do componente *i* na mistura, X_m é fração molar de grupo do grupo *m*, τ_{mk} é o fator de Boltzmann e a_{mn} é o parâmetro de interação binário entre os grupos *m* e *n*, estimado a partir de dados experimentais. Larsen, Rasmussen e Fredenslund (1987) propuseram a substituição do termo combinatorial de Staverman-Guggenheim (Eq. 1.20) pelo de Flory-Huggins (Eqs. 1.31 e 1.32), com a fração volumétrica da molécula de acordo com Kikic e co-autores (1980). Além disso, o parâmetro a_{mn} de interação binário entre os grupos foram descritos através de uma relação não-linear, dependente da temperatura (Eq. 1.33). A partir destas modificações, os autores obtiveram melhores resultados na descrição do equilíbrio líquido-vapor de misturas de alcanos, especialmente quando a diferença entre o tamanho dos componentes é grande e observaram que o modelo modificado podia predizer o equilíbrio líquido-líquido com a mesma qualidade que o modelo UNIFAC original, sendo mais robusto em relação à dependência da temperatura.

$$\ln \gamma_i^c = \ln \frac{\varpi_i}{x_i} + 1 - \frac{\varpi_i}{x_i} \tag{1.31}$$

$$\varpi_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \tag{1.32}$$

$$a_{mk} = a_{mk,1} + a_{mk,2}\,(T-T_0) + a_{mk,3}\,(\,T \ln(T_0/T) + T - T_0) \tag{1.33}$$

onde ϖ_i é a fração volumétrica da molécula *i*, modificada, $a_{mk,1}$, $a_{mk,2}$ *e* $a_{mk,3}$ são os coeficientes para o cálculo do parâmetro de interação binário e T_0 é a temperatura referência (298,15 K). Contudo, em geral, sistemas alimentícios são compostos por misturas de eletrólitos, tais como ácidos fracos, sais, amino-ácidos e compostos voláteis que se dissociam em solução, produzindo espécies iônicas responsáveis por interações moleculares que não são levadas em consideração nos modelos de composição local como o UNIFAC. Além da literatura da área de alimentos, pesquisas relacionadas ao tratamento de resíduos, como as separações por membranas ou neutralização controlada do pH, bem como estudos dos processos geológicos ou da engenharia de materiais vêm demonstrando interesse pela modelagem de soluções de eletrólitos. Em 1923, Debye e Hückel propuseram um modelo para o cálculo do coeficiente de atividade ($\gamma_i{*}^{LR}$) que levasse em consideração as denominadas *forças de longo-alcance*, interações eletrostáticas inversamente proporcionais ao quadrado da distância entre dois íons e que contribuem para a não-idealidade do sistema. Porém, como a teoria destes autores é aplicada para sistemas diluídos, Pitzer (1980) propôs extensões ao modelo de Debye-Hückel para que a teoria pudesse ser utilizada em soluções de eletrólitos mais concentradas (Eq. 1.34).

$$\ln\gamma_i^{*LR} = -\left(\frac{1000}{M_s}\right)^{0.5} A_\Phi \left[\left(\frac{2z_i^2}{17.1}\right)\ln\left(1+17.1I_x^{0.5}\right)+\frac{\left(z_i^2 I_x^{0.5}-2I_x^{1.5}\right)}{\left(1+17.1I_x^{0.5}\right)}\right] \tag{1.34}$$

onde M_s é a massa molar da água, A_Φ é o parâmetro de Debye-Hückel (A_Φ = 1,40060814 . 10^6 $d_s^{0,5}$ ($D_s T$)$^{-1,5}$), d_s é a densidade do solvente (g cm^{-3}), D_s é a constante dielétrica do solvente (Ds = -31,61 + 32733,43 T^{-1}), T é a temperatura (K), z_i é a carga do íon e I_x é a força iônica da solução ($I_x = (½)\ \Sigma\ x_i z_i^2$). Quando as concentrações iônicas são pequenas, a distância média entre os íons é grande e neste caso, somente as forças eletrostáticas de *longo-alcance* são importantes. Porém, quando a concentração da solução aumenta, os íons começam a interagir também com forças repulsivas e atrativas denominadas interações de *curto alcance*, ou forças de van der Waals. Desta forma, para calcular os coeficientes de atividade de soluções contendo eletrólitos, a literatura começou a utilizar modelos de composição local para a representação das interações de *curto-alcance* e um termo de Debye-Hückel para representar as interações de *longo-alcance*. Dentre os diversos estudos relacionados às soluções de eletrólitos, Achard, Dussap e Gross (1994) resolveram aplicar o modelo UNIFAC modificado por Larsen e co-autores (1987) e a forma modificada da equação de Debye-Hückel, proposta por Pitzer (1980) para a predição do pH de soluções ácidas e salinas. O cálculo do coeficiente de atividade das espécies, portanto, foi obtido através da somatória dos resultados expressos pelos dois modelos, conforme a equação 1.35.

$$\ln \gamma_i^* = \ln \gamma_i^{*SR} + \ln \gamma_i^{*LR} \tag{1.35}$$

onde γ_i^* é o coeficiente de atividade assimétrico da espécie i, γ_i^{*LR} é o termo que descreve as interações de *longo-alcance*, calculado a partir da equação de Debye-Hückel modificada por Pitzer (1980) e γ_i^{*SR} é o termo que descreve as interações de *curto-alcance*, na escala assimétrica, calculado a partir do modelo UNIFAC-Lyngby (LARSEN; RASMUSSEN;

FREDENSLUND, 1987). De modo que a convenção adotada para o cálculo do coeficiente de atividade pelo método UNIFAC, γ_i^{SR}, é a simétrica, ou seja, o estado padrão de cada componente *i* da solução é tido como a solução pura de *i* à temperatura da solução ($\gamma_i \rightarrow 1$ quando $x_i \rightarrow 1$) o termo relacionado às forças de *curto-alcance* na escala assimétrica, γ_i^{*SR}, é calculado pela equação 1.36.

$$\ln \gamma_i^{*SR} = \ln \gamma_i^{SR} - \ln\left(\lim_{x_i \to 0} \gamma_i^{SR}\right) \tag{1.36}$$

Além disso, Achard, Dussap and Gross (1994) propuseram a utilização de equações que levassem em conta o fenômeno de solvatação entre a água e as espécies iônicas. Estas equações estão baseadas na definição do número de hidratação de cada íon, que corresponde ao número de moléculas de água que estão quimicamente ligadas com as espécies carregadas. Deste modo, os parâmetros de interação do termo combinatorial do modelo UNIFAC-Lyngby e as frações molares dos compostos são modificados de acordo com as equações 1.37 a 1.39 e o termo relativo às interações de *curto-alcance* calculado através da equação 1.40.

$$x_1^H = \frac{x_1 - \sum_{k=2} Nh_k x_k}{1 - \sum_{k=2} Nh_k x_k} \tag{1.37}$$

$$x_i^H = \frac{x_i}{1 - \sum_{k=2} Nh_k x_k} \tag{1.38}$$

$$R_k^H = R_k + Nh_k R_1 \tag{1.39}$$

$$\gamma_i^{SR} = \frac{\gamma_i^{SR,H} x_i^H}{x_i (\gamma_1^{SR,H} x_1^H)^{-Nh_i}} \tag{1.40}$$

onde o subscrito *1* refere-se à água, o sobre-escrito *H* refere-se à condição de hidratação, Nh_k representa o número de hidratação do íon *k* à diluição infinita e x_i é a fração molar de *i*.

Diversos autores vêm utilizando o modelo UNIFAC-Lyngby e a equação de Debye-Hückel modificada por Pitzer (1987) na predição de propriedades de equilíbrio de soluções compostas por substâncias da área de alimentos. Achard, Dussap e Gros (1994), através deste modelo combinado, estudaram o pH de ácidos orgânicos à 25 ºC, Velezmoro (1999) e Oliveira (2005) corrigiram alguns parâmetros de interação e avaliaram a atividade de água e o pH de soluções de ácidos policarboxílicos à 25 ºC, Kuramoshi e co-autores (1997) estudaram o coeficiente de atividade de soluções de aminoácidos e Ninni e Meirelles (2001), o pH, a densidade e o coeficiente de atividade de sistemas aquosos e não aquosos dos mesmos compostos. Achard, Gros e Dussap (1992) utilizaram o modelo UNIFAC-Lyngby no estudo do equilíbrio líquido-vapor de soluções não-eletrolíticas de açúcar à pressão ambiente; Catté e co-autores (1994), Catté, Dussap e Gros (1995) e Peres e Macedo (1996, 1997) avaliaram o equilíbrio de fases de soluções aquosas e não aquosas de açúcares à pressão ambiente através de abordagens distintas relacionadas à estrutura molecular dos compostos e à dependência da temperatura dos parâmetros de interação. Em geral, esses trabalhos obtiveram bons resultados na avaliação do equilíbrio de fases utilizando o modelo UNIFAC-Lyngby e introduzindo a equação modificada de Debye-Hückel proposta por Pitzer (1980) no estudo de soluções eletrolíticas.

Contudo, embora a literatura relate inúmeros estudos na área, os modelos termodinâmicos para a predição do coeficiente de atividade de soluções de eletrólitos e não eletrólitos na área de alimentos ainda necessitam de inúmeros estudos. Gros e Dussap (2003) utilizaram o modelo UNIFAC-Lyngby e a equação modificada de Debye-Hückel (PITZER, 1980) na estimativa de propriedades de equilíbrio (atividade de água, pH, pressão osmótica e acidez) de misturas modelo para meios de fermentação (utilizados na produção de vinagre), bebidas isotônicas e leite, solução tampão de citrato (utilizada para estabilizar o pH de bebidas) e solução tampão de bicarbonato (utilizada em processos de carbonatação). A comparação com as medidas experimentais apresentou resultados proporcionais à simplificação dos referidos modelos e a ausência de parâmetros de interação binária mais precisos. Román-Leshkov e co-autores (2007) apresentaram um trabalho muito interessante sobre a conversão de D-frutose a 2,5-dimetilfurano (DMF) (produto da reação de *Maillard*) como potencial líquido combustível. Eles utilizaram a extração líquido-líquido com HCl, NaCl e solvente alcoólico, hidrogenação do extrato via processo catalítico e por fim um processo de separação líquido-vapor para obtenção do produto final. A predição das propriedades de equilíbrio dos sistemas citados através de um modelo semiempírico como o UNIFAC-Lyngby e a equação modificada de Debye-Hückel proposta por Pitzer (1980) poderia otimizar o planejamento utilizado pelos autores.

Por fim, Gmehling (2009), em revisão publicada recentemente, salienta que, para o desenvolvimento de equações de estado, modelos de contribuição de grupos e modelos de eletrólitos, são necessários dados de coeficientes de atividade, coeficientes osmóticos, pressão de vapor e propriedades críticas. Estes bancos de dados podem ser aplicados para determinar parâmetros ótimos no desenvolvimento de processos, verificar os parâmetros antes das simulações ou selecionar solventes para processos de destilação, extração e absorção.

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CAPÍTULO 2

Boiling point of aqueous D-glucose and D-fructose solutions: Experimental determination and modeling with group contribution method

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Trabalho a ser submetido para a revista *Fluid Phase Equilibria*

Boiling point of aqueous D-glucose and D-fructose solutions: Experimental determination and modeling with group contribution method

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Abstract

Boiling points of aqueous solutions affect the design and operation of evaporators. Hence, boiling points of aqueous solutions of D-glucose and D-fructose were experimentally determined at soluble solute concentration from 10 to 60 % by mass and pressure from 20 to 93.6 kPa. The experimental data were correlated with data predicted by the calculation of the activity coefficients with the UNIFAC-Lyngby model using different approaches for decomposition of the molecular structure: the aliphatic groups and the cyclic groups. Moreover, the rise in experimental boiling point of the aqueous sugar solutions was evaluated by the Dühring's rule. It was observed that the cyclic approach resulted in better accuracy for liquid-vapor equilibrium prediction and the non-ideality of these solutions are relevant in the boiling point rise, confirming that the rise in boiling point of aqueous D-glucose and D-fructose concentrated solutions is significant to the design of heat and mass transport operations.

Key-words: UNIFAC, Dühring, glucose, fructose, boiling point

2.1 Introduction

According to the review of Starzak and Mathlouthi [1], the vapor-liquid equilibrium (VLE) and colligative property data (boiling point, freezing point, vapor pressure and osmotic pressure) of carbohydrates solutions have been reported in literature since the nineteenth century. Special attention is given to the evaluation of thermophysical properties of aqueous sugar solutions because carbohydrates are the main components of several food liquids such as sugar syrups, fruit juices and other beverages, whose properties affect the design and operation of several industrial processes.

Recent studies have given special attention to the calculation of thermophysical properties using predictive models. The UNIFAC-Lyngby model [2] is a widely used modified UNIFAC group-contribution method [3] that predicts the activity coefficient of a specie in a solution. According to this model, the activity coefficient can be written as the sum of a combinatorial contribution, which accounts for size and shape effects, and a residual contribution, which accounts for interactions among groups (Eqs. 2.1 to 2.10). The UNIFAC-Lyngby model modifies the Staverman-Guggenheim combinatorial term of the original UNIFAC model and introduces the modified ($r^{2/3}$) Flory-Huggins combinatorial term. This modification is considered to be much better at describing the VLE of alkane mixtures, especially when the difference in size of the components is large [2]. Also, the group-interaction parameters of the residual term are temperature-dependent.

$$ln\ \gamma_i = ln\ \gamma_i^c + ln \gamma_i^r \tag{2.1}$$

$$\ln \gamma_i^c = \ln \frac{\varpi_i}{x_i} + 1 - \frac{\varpi_i}{x_i} \tag{2.2}$$

$$\ln \gamma_i^r = \sum_{k=1}^{n} v_k^i \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \tag{2.3}$$

$$\varpi_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \tag{2.4}$$

$$r_i = \sum_{k=1}^{n} v_k^{(i)} R_k \tag{2.5}$$

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_{m=1}^{n} \Psi_m \tau_{mk} \right) - \sum_{i=1}^{n} \frac{\Psi_i \tau_{ki}}{\sum_{j=1}^{n} \Psi_j \tau_{ji}} \right] \tag{2.6}$$

$$\Psi_m = \frac{Q_m X_m}{\sum_{p=1}^{n} Q_p X_p} \tag{2.7}$$

$$X_m = \frac{\sum_{j=1}^{n} v_m^{(j)} x_j}{\sum_{j=1}^{n} \sum_{p=1}^{n} v_p^{(j)} x_j} \tag{2.8}$$

$$\tau_{mk} = \exp\left(\frac{-a_{mk}}{T} \right) \tag{2.9}$$

$$a_{mk} = a_{mk,1} + a_{mk,2}\ (T - T_0) + a_{mk,3}\ (\ T\ ln(T_0/T) + T - T_0) \tag{2.10}$$

where γ_i is the symmetrical activity coefficient of molecule i, γ_i^c is the combinatorial term and γ_i^r is the residual term, x_i is the molar fraction, ω_i is the volume fraction of molecule i, r_i is the molecular volume parameter, v_{ki} is the number of k type groups in molecule i, Γ_k is the activity coefficient of group k in mixed composition, Γ_k^i is the activity coefficient of group k for a group composition corresponding to the pure component i, Ψ_i is the surface area fraction of component i in mixture, X_m is the group mole fraction of group m and τ_{mk} is the Boltzmann factor. The structural parameters R_k and Q_k for the groups and the temperature-dependent group-interaction parameters a_{mk} are obtained from properties data tables. T is the temperature (K) and T_0 is the reference temperature (298.15 K).

Several authors used the UNIFAC-Lyngby model and concluded that this model is able to accurately predict the boiling temperature and other colligative properties of aqueous sugar solutions. However, since chemical groups described by Larsen et al. [2] do not account for cyclic conformation and tautomerism of carbohydrate molecules, different approaches were encountered in literature to better describe the thermodynamic equilibrium behavior of these kinds of molecules. Achard et al. [4] used the aliphatic alkanes and ether groups for the prediction of experimental boiling point data for aqueous sugar solutions and presented good agreement with experimental normal boiling point. Kuramoshi et al. [5] extended the utilization of aliphatic groups and introduced a new group composed of the portion containing asymmetric carbon atoms of the aldohexose molecule for the evaluation of the activity coefficient of aqueous sugar systems. Catté et al. [6] introduced three new main groups (pyranose ring, furanose ring and osidic bond) to describe the carbohydrate molecules allowing distinction of molecular isomers, and has set non-linear temperature-dependent interaction parameters; Peres and Macedo [7] used these new groups, introduced the OH_{ring} due to proximity effects and adjusted the temperature-independent interaction parameters from normal boiling point data, obtaining relative deviations from experimental data of approximately 1 %. Catté et al. [8] described the molecules of D-glucose, D-fructose and sucrose as unique groups and determined non-linear temperature-dependent interactions parameters. Peres and Macedo [9] estimated linear temperature-dependent parameters from normal boiling point data using the same approach and obtained root mean square deviations of approximately 2.5 % for binaries systems composed of water + carbohydrate (sucrose, D-glucose and D-fructose).

Although the boiling point of aqueous sugar solutions have already been studied for binary and multicomponent solutions at different concentrations, limited information is available on the boiling point of monosaccharides such as D-glucose and D-fructose at different pressures. Thus, the aim of this study was to determine the boiling point of sugar solutions (D-glucose and D-fructose) as a function of pressure and soluble solute content and correlate the experimental data with that predicted by the calculation of the activity coefficient with the UNIFAC-Lyngby model data using the aliphatic chemical groups [2], the cyclic chemical groups and new oxygenate groups of Peres and Macedo [7] and considering the whole molecule as a unique group [9]. The rise in experimental boiling point of the aqueous sugar solutions was evaluated by the Dühring's rule and a thermodynamic evaluation was also proposed for the best approach.

2.2 Material and Methods

Sucrose, D-glucose and D-fructose were supplied by Merck (USA) with purity greater than 99 % by mass. Binary solutions (sugar + water) were prepared gravimetrically with deionized water (Millipore, USA) using a semi-analytical balance (Marte, Brazil) with precision of $1x10^{-2}$ g.

The experimental boiling point data of the binaries mixtures D-glucose + water and D-fructose + water were determined at soluble solute concentration from approximately 10 to 60 % by mass and pressure from 20 to 93.6 kPa. For this purpose, the vapor-liquid equilibrium (VLE) of the systems was obtained using a modified rotary evaporator

(Marconi, Brazil) with total reflux of the vapor phase (Fig. 2.1). In each experiment, a 500 mL sample of the sugar + water mixture was introduced into the boiling rotary vessel, which was heated by a silicon oil bath. The system pressure was adjusted by a vacuum pump (Marconi, Brazil) and monitored with a 0.1 mmHg precision U-type mercury manometer. A vessel was used between the pump and the apparatus to avoid variations of the pressure. A thermostated water bath (VT2 Anton Paar, Austria) was used to cool the condenser fluid at 288.15 ± 0.1 K to increase the driving force for the condensation of the vapor phase. The temperature difference between the silicon oil bath and the boiling solution was maintained at approximately 283.15 K for maintenance of the driving force for evaporation. The solution was kept under evaporation until equilibrium was reached (constant T and P). The temperature of the binary mixture was measured by a calibrated 0.1 K precision PT-100 sensor and concentration of the liquid phase (ºBrix at 293.15 K) was measured using a calibrated digital density meter (DMA 4500 Anton Paar, Austria) to verify concentration during the experiment. The procedure was repeated up to atmospheric pressure (93.6 ± 0.1 kPa, according to Ref. [10]), allowing measurements of boiling points at different pressures with the same mixture concentration.

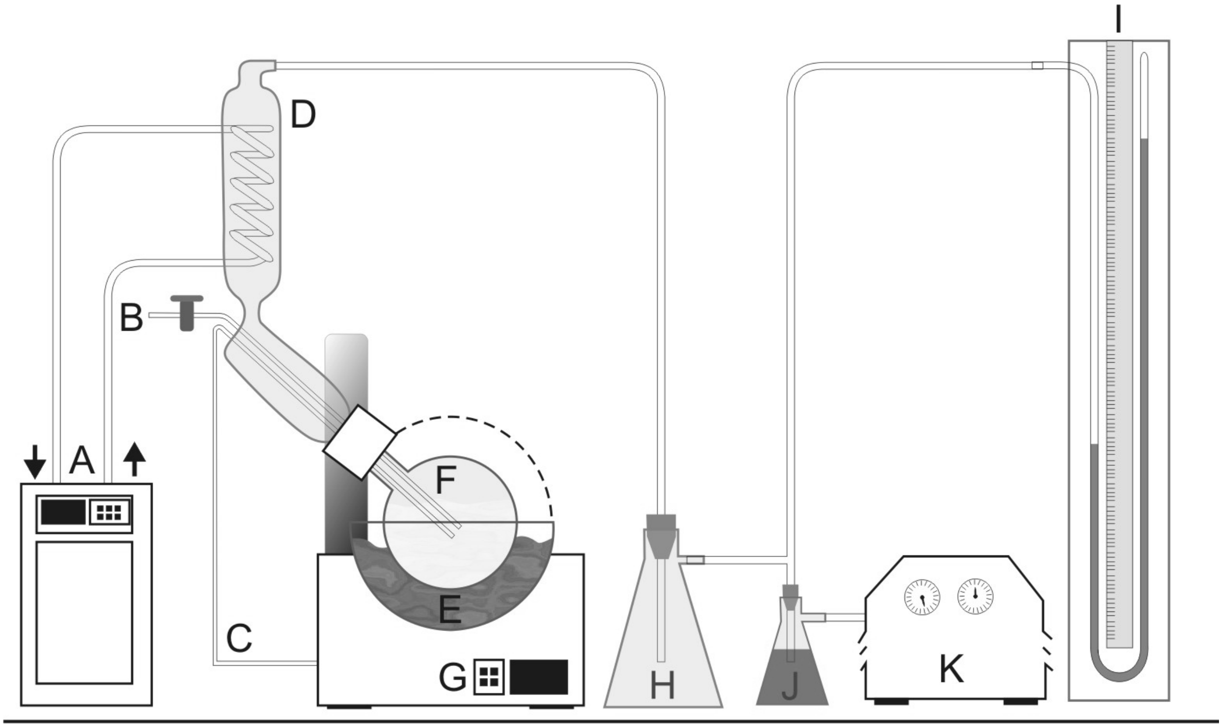

Fig. 2.1. System used for boiling point measurement: (A) thermostated water bath (VT2 Anton Paar, Austria), (B) sample collector, (C) PT-100 sensor, (D) condenser, (E) silicon oil bath, (F) boiling rotary vessel, (G) temperature controller, (H) vessel to avoid pressure variations, (J) security vessel, (K) vacuum pump (Marconi, Brazil), (I) U-type mercury manometer.

Modeling of the measured boiling point data was carried out evaluating the VLE data of the systems. If the condition for thermodynamic equilibrium is the equality of the chemical potentials (μ_i) of the species between the two phases, accounting for the non-volatility of the solutes in the formulated binaries (sugar + water) and assuming that the pressures are low enough to treat the vapor phase as ideal, the system pressure is given by Eq. (2.11).

$$P = P_w = x_w \, \gamma_w P^{vap}{}_w \tag{2.11}$$

where P_w is the partial pressure of water, x_w is the molar fraction of water and $P^{vap}{}_w$ is the vapor pressure of the pure water at the estimated boiling temperature. The dependence of $P^{vap}{}_w$ (mmHg) on temperature (T / ºC) was expressed by Antoine's equation (Eq. 2.12) whose parameters were taken from Ref. [11]. The activity coefficient of water γ_w was calculated by the UNIFAC-Lyngby model.

$$log_{10} P^{vap}_w = 8.071 - 1730.6\,(t + 233.4)^{-1} \tag{2.12}$$

For the prediction of γ_i, the sugar molecules were decomposed according to 3 approaches: i) using the aliphatic alkane and ether groups for the composition of the cyclic carbohydrates; ii) using the groups proposed by Peres and Macedo [7] with temperature-independent interaction parameters and iii) using the approach of Peres and Macedo [9], that considers the whole molecule as a unique group. Table 2.1 presents the chemical structure of the carbohydrate according to the first [2] and second approaches [9] used in this work. Table 2.2 shows the UNIFAC-Lyngby structural (R_k and Q_k) and interaction parameters ($a_{mk,i}$) according to Ref. [2], Table 2.3 shows the UNIFAC parameters according to Peres and Macedo [7] and Table 2.4 shows the UNIFAC parameters according to Peres and Macedo [9].

Table 2.1
UNIFAC groups of the carbohydrates

	Larsen et al. [2]					Peres and Macedo [7]					
Molecules	CH_2	CH	C	OH	CH–O	PYR	FUR	–O–	CH_2	OH_{ring}	H_2O
D-glucose	1	4	0	5	1	1	0	0	1	5	0
D-fructose	2	2	1	5	1	0	1	0	2	5	0
Sucrose	3	5	1	8	3	1	1	1	3	8	0
Water	0	0	0	0	0	0	0	0	0	0	1

Table 2.2
UNIFAC structural and interaction parameters [2]

Structural Parameters			Interaction parameters $a_{mk,i}$ (each row gives one coefficient of Eq. 2.10: $a_{mk,1}$, $a_{mk,2}$, $a_{mk,3}$))				
				k			
Group	R_k	Q_k	*m*	CH_2	OH	H_2O	CH–O
CH_2	0.6744	0.5400	CH_2	0.0	972.8	1857.0	230.5
CH	0.4469	0.2280		0.0	0.2687	-3.322	-1.328
C	0.2195	0.0000		0.0	8.773	-9.000	-2.476
OH	1.0000	1.2000	OH	637.5	0.0	155.6	227.0
				-5.832	0.0	0.3761	1.364
				-0.8703	0.0	-9.000	3.324
H_2O	0.9200	1.4000	H_2O	410.7	-47.15	0.0	19.54
				2.868	-0.4947	0.0	1.293
				9.000	8.650	0.0	-8.850
CH–O	0.6908	0.468	CH–O	369.9	137.1	183.1	0.0
				-1.542	-1.115	-2.507	0.0
				-3.228	-4.438	0.0	0.0

Table 2.3
UNIFAC structural and interaction parameters [7]

Structural Parameters			Interaction parameters $a_{mk,1}$ (Eq. 2.10) $a_{mk,2}$ and $a_{mk,3}$ were set to zero						
				k					
Group	R_k	Q_k	*m*	CH_2	PYR	FUR	–O–	OH_{ring}	H_2O
CH_2	0.6744	0.540	CH_2	0.0	0.0	0.0	0.0	0.0	0.0
PYR	2.4784	1.562	PYR	0.0	0.0	0.0	0.0	0.0	-43.27
FUR	2.0315	1.334	FUR	0.0	0.0	0.0	0.0	0.0	-169.23
–O–	1.0000	1.200	–O–	0.0	0.0	0.0	0.0	0.0	0.0
OH_{ring}	0.2439	0.442	OH_{ring}	0.0	0.0	0.0	0.0	0.0	591.93
H_2O	0.9200	1.400	H_2O	0.0	-599.04	-866.91	0.0	-102.54	0.0

Table 2.4
UNIFAC structural and interaction parameters [9]

Structural Parameters			Interaction parameters $a_{mk,i}$ (each row gives one coefficient of Eq. 2.10: $a_{mk,1}$, $a_{mk,2}$, $a_{mk,3}$)				
				k			
Group	R_k	Q_k	m	D-glucose	D-fructose	Sucrose	H_2O
D-glucose	8.1528	7.920	D-glucose	0.0	0.0	0.0	-68.6157
				0.0	0.0	0.0	-0.0690
				0.0	0.0	0.0	0.0
D-fructose	8.1529	8.004	D-fructose	0.0	0.0	0.0	-28.2892
				0.0	0.0	0.0	1.7780
				0.0	0.0	0.0	0.0
Sucrose	14.5496	13.764	Sucrose	0.0	0.0	0.0	-89.3391
				0.0	0.0	0.0	0.3280
				0.0	0.0	0.0	0.0
H_2O	0.9200	1.400	H_2O	96.5267	42.3676	118.9952	0.0
				0.2770	-2.2511	-0.3410	0.0
				0.0	0.0	0.0	0.0

According to Catté et al. [6], the pyranose (PYR) and the furanose (FUR) groups are the cyclic rings of the hexose and pentose structures of D-glucose and D-fructose, respectively (Fig. 2.2) and the osidic bound (–O–) group is the ether group of sucrose molecule. According to Peres and Macedo [7], the OH_{ring} group represents the hydroxyl groups that appear in the monosaccharide molecule and present specific interactions because they are very close to each other.

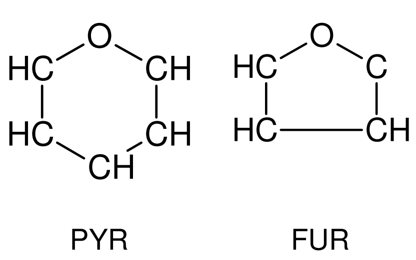

Fig. 2.2. Pyranose (PYR) and furanose (FUR) groups

Because γ_i and $P^{vap}{}_w$ are temperature-dependent, an optimization algorithm was implemented in MATLAB 7.0 based on the Quasi-Newton method (MATLAB function *fmincon*) for calculation of the minimum of an objective function. The objective function was the absolute deviation (*AD*) (Eq. 2.13) between experimental pressure P of the system and the calculated pressure P_{calc} (Eq. 2.11). Figure (2.3) shows the flowchart of the implemented algorithm.

$$AD = P - P_{calc} = P - x_w \gamma_w P^{vap}{}_w \qquad (2.13)$$

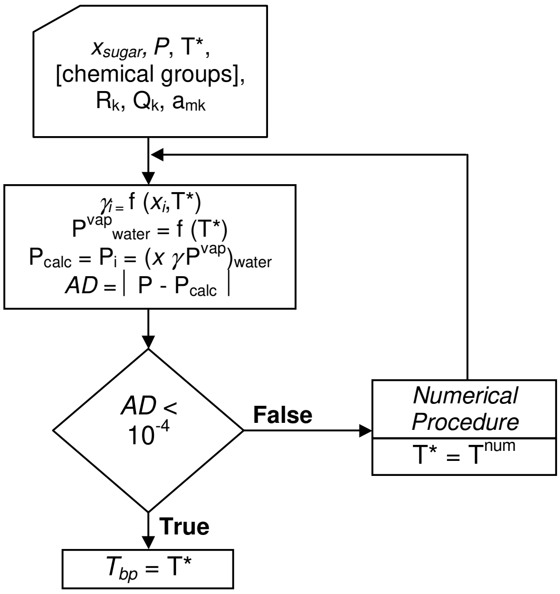

Fig. 2.3. Algorithm for calculation of the boiling point. x_{sugar} is the molar fraction of the carbohydrate in the considered binary mixture, P is the experimental pressure of the system, T_0 is the initial guess for boiling temperature calculation, P_{calc} is the calculated pressure, *AD* is the absolute deviation between P and P_{calc}, T^{num} is a new value of T* and T_{bp} is the boiling temperature.

The first step of the procedure was the recognition of the principle variables, stated as the molar fractions x_i of the binary mixture, the pressure P of the considered system, the molecular chemical groups in the solution (according to each approach) and the group structural and interaction parameters, R_k, Q_k and a_{mk} obtained from the database of the aforementioned literature. Initial iteration started with a boiling temperature value, T^*, sufficiently close to the optimal solution and taken from the boiling point of distillated water at the same pressure P. The activity coefficient γ_i and the partial pressure P_i of the solvent were calculated to construct the objective function (Eq. 2.13). The minimum of the function was found with a Quasi-Newton method with values of absolute deviation (AD) less than 10^{-4}.

2.3 Results and Discussion

2.3.1 Performance of the methodology

To check the performance of the apparatus, experimental data of pure distillated water and sucrose + water mixtures at various concentrations and pressures were compared with data found in literature [12-15] (Fig. 2.4). For this purpose, data from literature were interpolated by cubic spline interpolation with an algorithm implemented in MATLAB 7.0. The experimental boiling point of pure distillated water was measured from 18.7 to 93.6 kPa and VLE data of sucrose + water mixtures were measured at 31.2, 47.3, 71.2 and 84.5 kPa and 35.2, 51.6, 60.2 and 75.8 % sugar by mass at each pressure. Agreement between experimental and reported data was good, since the fitted curve (continuous line of Fig. 2.4), determined by linear regression, presented only slight deviation from the straight diagonal line.

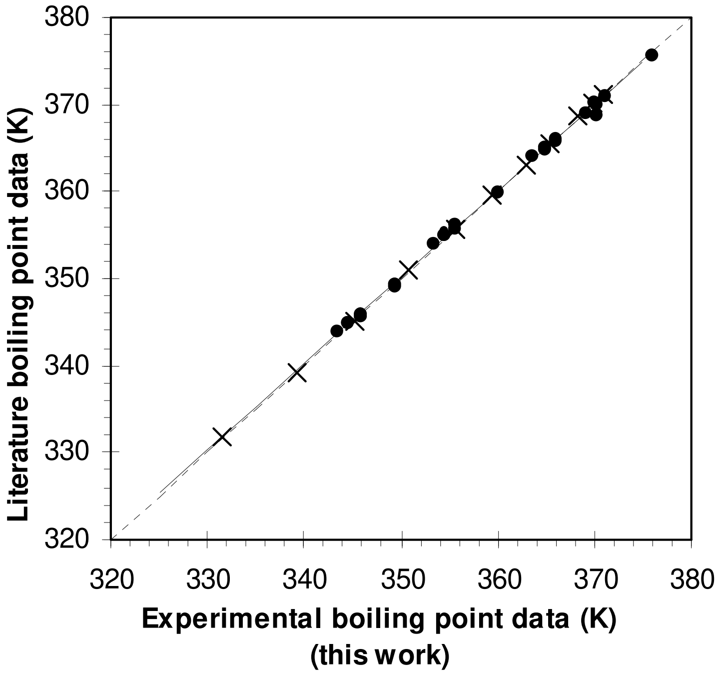

Fig. 2.4. Experimental (this work) versus boiling point data from literature of (•) sucrose+water mixtures [12-14] and (x) pure distillated water [15]. Dashed line represents the straight diagonal line and the continuous line is the curve fitted with the data ($y = 0.987 x + 4.552$, $r^2 = 0.9986$). Number of observations = 48.

For evaluation of the performance of the algorithm, activity coefficients of methanol + water mixtures at 25 ºC were predicted with the algorithm implemented in this work and compared with data presented by Ref. [11] (Table 5). Moreover, the boiling point of sugar + water mixtures at 760 mmHg calculated in this work, according to Peres and Macedo [7] approach, using the UNIFAC-Lyngby model, were compared with experimental data presented by Abderafi and Bounahmidi [16]. The average relative deviations $\sigma(\%)$ of the predicted data in this work (D_{work}) from data found in literature (D_{liter}) were calculated according to Eq. (2.14) where n is the number of observations.

$$\sigma(\%) = 100 \left(\Sigma_n \mid D_{liter} - D_{work} \mid / D_{liter} \right) n^{-1} \tag{2.14}$$

The agreement between data from literature and that predicted in this work was good in both cases, since $\sigma(\%)$ was less than 1 %. The deviation observed in Table 5 was likely due to the fact that VLE of methanol + water presented by Ref. [11] was predicted using the UNIFAC model with the Staverman-Guggenheim combinatorial term. Good agreement between the experimental boiling point data presented by Abderafi and Bounahmidi [16] for sugar + water mixtures at 760 mmHg and the data predicted in this work suggested the accuracy of the implemented algorithm as well as the predictability of the UNIFAC-Lyngby model as shown by Peres and Macedo [7]. Moreover, the value of $\sigma(\%)$ presented by this author was close to that presented in this work (0.52 % for D-glucose + water mixtures, 1.48 % for D-fructose + water mixtures and 0.56 % for sucrose + water mixtures). The difference between the $\sigma(\%)$ values is due to the numerical method used for boiling point calculation. Also, in order to compare the data from literature with the data obtained in this work, some units are in mmHg and ºC.

Table 2.5
Comparison of the VLE and activity coefficients for methanol(1)-water(2) presented by Ref. [11] and calculated in this work at 25 ºC.

	Literature [11]					This work			
x_1	y_1	P (mmHg)	γ_1	γ_2		y_1	P (mmHg)	γ_1	γ_2
0.0	0.000	23.7	2.24	1.00		0.000	23.6	2.24	1.00
0.1	0.508	43.9	1.75	1.01		0.507	43.7	1.75	1.01
0.2	0.655	57.3	1.47	1.04		0.654	57.0	1.47	1.04
0.3	0.734	67.8	1.30	1.09		0.733	67.5	1.30	1.09
0.4	0.789	77.0	1.19	1.14		0.789	76.5	1.19	1.14
0.5	0.834	85.5	1.12	1.20		0.833	85.0	1.12	1.20
0.6	0.872	93.7	1.07	1.27		0.871	93.2	1.07	1.27
0.7	0.906	102.0	1.03	1.34		0.906	101.4	1.03	1.34
0.8	0.939	110.3	1.01	1.42		0.939	109.6	1.01	1.42
0.9	0.970	118.9	1.00	1.51		0.970	118.1	1.00	1.51
1.0	1.000	127.7	1.00	1.60		1.000	126.9	1.00	1.60
					$\sigma(\%)$ =	*0.06*	*0.53*	*0.20*	*0.18*

Table 2.6
Comparison of experimental [16] and predicted normal boiling point data using the UNIFAC-Lyngby model [7]. w_1, % by mass and σ (%) is the relative deviation of predicted from experimental data.

D-glucose(1) + water(2)			D-fructose(1) + water(2)			Sucrose(1) + water(2)		
w_1	Experimental	Predicted	w_1	Experimental	Predicted	w_1	Experimental	Predicted
4.5	100.2	100.2	4.5	100.1	100.2	5.6	100.1	100.1
5.5	100.4	100.2	6.0	100.3	100.2	10.6	100.3	100.2
10.5	100.6	100.4	9.5	100.4	100.3	21.5	100.4	100.4
12.0	100.7	100.4	11.5	100.6	100.4	32.0	101.2	100.7
21.0	101.3	100.8	20.5	101.1	100.8	44.5	101.8	101.3
25.0	101.4	101.0	25.5	101.2	101.1	59.6	103.0	102.8
33.5	101.6	101.6	34.0	101.3	101.7	65.0	104.0	103.8
41.0	101.8	102.3	46.0	102.5	102.8	76.0	108.2	107.6
45.0	103.0	102.7	58.5	104.9	105.0	78.5	110.0	109.1
55.5	104.0	104.3	68.0	108.4	107.9	82.0	115.0	112.1
64.0	106.0	106.4	82.0	122.0	117.8	86.5	118.0	118.1
81.5	107.7	117.2	87.0	130.0	125.9			
	σ(%) =	*0.99*		*σ(%) =*	*0.72*		*σ(%) =*	*0.51*

2.3.2 Experimental and predicted boiling point data

First, for validation of the experimental measurements, the reproducibility of the data and the equilibrium time were checked by preparing 1500 mL of 10.3 % aqueous D-fructose solution (by mass). Three repetitions of boiling point data for a 500 mL sample were taken ranging from 20 kPa to atmospheric pressure. At each pressure, the mixture was maintained for a period of 1 h and the solutes concentration of the liquid-phase was measured. The mean-standard deviation of the boiling point measurements (0.06 K) was less than the precision of the temperature sensor (0.1 K) and the methodology could be considered reproducible. It was verified that, approximately 20 min after the pressure stabilized there was no variation of temperature and equilibrium was reached. A slight variation in the liquid-phase concentration was also observed during the experiment. However, because the standard-deviation of the concentration measurements (0.05 % sugar by mass) mwas less than 0.5 % of the mean-value (10.37 % sugar by mass), it was considered that the methodology and the apparatus were efficient for the purpose of this work.

Tables 2.7 and 2.8 show the experimental boiling point data of D-glucose + water and D-fructose + water mixtures and the data predicted by ideal assumption ($\gamma_i = 1$) and by the UNIFAC-Lyngby model using the classical aliphatic groups, the cyclic groups used by Peres and Macedo [7] and considering the molecule as a unique group [9]. As expected, the boiling point of aqueous D-glucose and aqueous D-fructose solutions increased with the increase of pressure and sugar concentration. The addition of a non-volatile in a solvent lowers the partial pressure of the solvent. As a consequence, the solution requires a higher temperature for the elevation of the partial pressure in the system to cause boiling. The added solute therefore increases the boiling point which obviously contributes to a concentration elevation [17].

Table 2.7
Boiling point data (K) for the binary system D-glucose(1) + water(2): w1 in % by mass (exp.) experimental data; (id.) ideal assumption; (A) aliphatic groups [2]; (B) Peres and Macedo [9]; (C) Peres and Macedo [7]

w_1	exp.	id.	(A)	(B)	(C)	w_1	exp.	id.	(A)	(B)	(C)	w_1	exp.	id.	(A)	(B)	(C)
20.0 kPa						26.7 kPa						33.3 kPa					
10.2	333.9	333.5	333.5	333.5	333.6	10.2	340.2	339.9	339.9	339.9	340.0	10.3	345.6	345.0	345.0	345.0	345.1
20.3	334.4	333.8	333.8	333.8	334.0	20.3	340.7	340.2	340.1	340.2	340.3	20.2	346.2	345.3	345.3	345.3	345.5
28.0	334.3	334.1	334.0	334.1	334.3	28.7	340.8	340.5	340.4	340.6	340.7	28.9	346.1	345.7	345.6	345.7	345.9
39.1	335.0	334.6	334.5	334.8	335.0	39.1	341.1	341.0	340.8	341.2	341.4	39.3	346.7	346.2	346.0	346.4	346.6
49.2	336.1	335.3	335.0	335.6	335.9	49.2	342.4	341.7	341.4	342.0	342.4	49.2	347.7	346.9	346.6	347.2	347.6
60.4	337.9	336.4	336.1	337.1	337.6	60.4	344.3	342.9	342.5	343.6	344.2	60.5	349.6	348.1	347.7	348.9	349.5
40.0 kPa						46.7 kPa						53.3 kPa					
10.3	349.9	349.3	349.3	349.3	349.5	10.3	353.7	353.1	353.1	353.1	353.2	10.3	357.0	356.4	356.4	356.4	356.5
20.2	350.4	349.7	349.6	349.7	349.8	20.2	354.4	353.4	353.4	353.5	353.6	20.2	357.7	356.8	356.7	356.8	356.9
29.0	350.7	350.0	349.9	350.1	350.3	28.9	354.0	353.8	353.7	353.9	354.0	28.8	357.4	357.1	357.0	357.2	357.4
39.5	350.7	350.6	350.3	350.7	351.0	39.4	354.9	354.4	354.1	354.5	354.8	39.3	358.1	357.7	357.5	357.9	358.1
49.3	352.3	351.3	351.0	351.6	352.0	49.3	355.7	355.1	354.8	355.4	355.8	49.4	359.2	358.5	358.1	358.8	359.2
60.5	354.1	352.5	352.1	353.3	353.9	60.5	357.6	356.4	356.0	357.2	357.7	60.6	361.0	359.8	359.4	360.6	361.2
60.0 kPa						66.7 kPa						73.3 kPa					
10.3	360.0	359.4	359.4	359.4	359.5	10.4	362.7	362.2	362.1	362.2	362.3	10.4	365.2	364.7	364.7	364.7	364.8
20.3	360.7	359.8	359.7	359.8	359.9	20.3	363.5	362.5	362.4	362.5	362.7	20.4	365.9	365.0	364.9	365.1	365.2
29.0	360.4	360.2	360.0	360.2	360.4	28.4	363.1	362.9	362.7	362.9	363.1	28.1	365.7	365.4	365.2	365.4	365.6
39.4	361.1	360.8	360.5	360.9	361.1	39.5	363.9	363.5	363.2	363.7	363.9	39.5	366.5	366.1	365.7	366.2	366.4
49.5	362.2	361.6	361.2	361.9	362.3	49.6	365.0	364.3	363.9	364.7	365.0	49.6	367.7	366.9	366.5	367.2	367.6
60.6	364.3	362.9	362.4	363.7	364.3	60.6	366.8	365.6	365.2	366.5	367.1	60.6	369.4	368.2	367.8	369.0	369.6
80.0 kPa						86.7 kPa						93.6 kPa					
10.4	367.4	367.0	367.0	367.0	367.1	10.4	369.5	369.2	369.2	369.2	369.3	10.5	372.0	371.3	371.3	371.3	371.4
20.4	368.1	367.4	367.3	367.4	367.5	20.5	370.3	369.6	369.5	369.6	369.7	20.6	372.7	371.7	371.6	371.7	371.8
27.8	367.6	367.7	367.5	367.8	367.9	28.5	370.3	369.9	369.7	370.0	370.1	29.2	372.6	372.1	371.9	372.2	372.3
39.5	368.9	368.4	368.1	368.5	368.8	39.5	371.2	370.6	370.3	370.7	371.0	39.5	373.3	372.8	372.4	372.9	373.1
49.6	370.1	369.2	368.8	369.6	369.9	49.6	371.9	371.4	371.0	371.8	372.1	49.6	374.5	373.6	373.2	374.0	374.3
60.8	371.8	370.6	370.2	371.5	372.1	60.9	374.2	372.9	372.4	373.7	374.3	61.0	376.6	375.1	374.6	375.9	376.5

Table 2.8

Boiling point data (K) of the binary system D-fructose(1) + water(2): w_1 in % by mass (exp.) experimental data; (id.) ideal assumption; (A) classical groups [2]; (B) Peres and Macedo [9]; (C) Peres and Macedo [7]

w_1	exp.	id.	(A)	(B)	(C)	w_1	exp.	id.	(A)	(B)	(C)	w_1	exp.	id.	(A)	(B)	(C)
20.0 kPa						26.7 kPa						33.3 kPa					
10.3	334.1	333.5	333.5	333.5	333.6	10.3	340.8	339.9	339.9	339.9	340.0	10.3	345.8	345.0	345.0	345.0	345.1
20.6	334.5	333.8	333.8	333.9	334.0	20.7	341.2	340.2	340.2	340.3	340.4	20.7	346.2	345.4	345.3	345.4	345.5
30.9	335.2	334.2	334.1	334.4	334.5	30.8	341.5	340.6	340.5	340.8	340.9	30.6	346.7	345.8	345.6	346.0	346.1
40.9	335.5	334.7	334.6	335.1	335.3	40.9	342.1	341.1	341.0	341.6	341.7	40.9	347.1	346.3	346.1	346.8	346.9
51.2	336.5	335.4	335.2	336.3	336.4	51.3	343.0	341.9	341.7	342.8	342.9	51.4	348.2	347.1	346.8	348.1	348.2
61.0	337.9	336.4	336.2	337.9	338.3	61.0	344.6	342.9	342.7	344.6	344.8	61.1	349.8	348.2	347.9	350.0	350.1
40.0 kPa						46.7 kPa						53.3 kPa					
10.3	350.0	349.3	349.3	349.4	349.5	10.3	353.9	353.1	353.1	353.1	353.2	10.3	357.2	356.4	356.4	356.5	356.5
20.8	350.6	349.7	349.6	349.8	349.9	20.9	354.4	353.5	353.4	353.6	353.6	20.9	357.8	356.8	356.7	356.9	357.0
30.7	351.1	350.1	350.0	350.4	350.4	30.8	355.0	353.9	353.7	354.2	354.2	30.8	358.3	357.2	357.1	357.5	357.5
40.9	351.4	350.7	350.5	351.2	351.2	40.9	355.4	354.5	354.2	355.1	355.0	41.1	358.5	357.9	357.6	358.5	358.4
51.5	352.5	351.5	351.2	352.6	352.6	51.6	356.4	355.3	355.0	356.5	356.4	51.6	359.7	358.7	358.4	359.9	359.8
61.1	354.2	352.6	352.3	354.5	354.6	61.2	358.0	356.5	356.2	358.5	358.5	61.2	361.4	359.9	359.5	362.0	361.9
60.0 kPa						66.7 kPa						73.3 kPa					
10.3	360.1	359.4	359.4	359.5	359.5	10.4	362.7	362.2	362.1	362.2	362.3	10.4	365.3	364.7	364.7	364.7	364.8
20.9	360.7	359.8	359.7	359.9	360.0	20.9	363.4	362.5	362.5	362.7	362.7	20.9	366.0	365.1	365.0	365.2	365.2
30.8	361.2	360.3	360.1	360.6	360.6	31.0	364.0	363.0	362.8	363.3	363.3	31.2	366.4	365.6	365.4	365.9	365.9
41.2	361.7	360.9	360.6	361.5	361.5	41.2	364.4	363.6	363.3	364.3	364.2	41.2	367.0	366.2	365.9	366.9	366.7
51.5	362.8	361.7	361.4	363.0	362.8	51.5	365.5	364.5	364.2	365.8	365.6	51.6	368.0	367.1	366.7	368.4	368.2
61.2	364.7	362.9	362.6	365.2	365.0	61.1	367.2	365.7	365.4	368.0	367.8	61.1	369.9	368.3	367.9	370.7	370.4
80.0 kPa						86.7 kPa						93.6 kPa					
10.4	367.7	367.0	367.0	367.0	367.1	10.4	369.8	369.2	369.2	369.2	369.3	10.4	372.1	371.3	371.3	371.3	371.4
21.0	368.2	367.4	367.3	367.5	367.6	21.0	370.5	369.6	369.5	369.7	369.7	21.1	372.8	371.7	371.6	371.9	371.8
31.2	368.7	367.9	367.7	368.2	368.2	31.2	370.8	370.1	369.9	370.4	370.4	31.2	373.2	372.2	372.0	372.6	372.5
41.0	369.0	368.5	368.2	369.2	369.1	40.9	371.3	370.7	370.4	371.4	371.3	41.3	374.2	372.9	372.5	373.7	373.4
51.8	370.4	369.5	369.1	370.9	370.6	51.9	372.8	371.7	371.3	373.2	372.8	52.0	375.1	373.9	373.4	375.4	375.0
61.0	372.2	370.7	370.3	373.1	372.7	60.8	374.3	372.8	372.5	375.3	374.9	61.2	376.7	375.1	374.7	377.7	377.2

The boiling points of D-fructose + water mixtures were slightly higher than that of D-glucose + water at the same pressure and soluble solutes concentration. In fact, Darros-Barbosa et al. [18] showed that, among the aqueous sugar solutions observed in this work, D-fructose + water mixtures have the strongest deviation from ideality at higher temperatures and concentrations and present a slightly higher heat capacity, probably related to the difference in isomeric composition of the equilibrium in aqueous solution and to its lower compatibility with water structure, presenting a more disturbed hydration layer. These observations highlight the isomeric approach of the aqueous sugar mixtures. In aqueous D-glucose solutions, the proportion of the pyranose tautomer is nearly temperature-independent and its concentration is approximately 99 % [19]. In aqueous D-fructose solutions, the proportions of pyranose and furanose tautomers are temperature-dependent but, at higher temperatures the proportion of the furanose tautomer is greater than the pyranose tautomer [20]. This reinforces the adopted group-decomposition for prediction of the boiling point of aqueous sugar solutions by the UNIFAC-Lyngby approaches used in this work, which took into account that D-glucose exists only as a pyranose tautomer and D-fructose exists only as a furanose tautomer.

The calculated mean-relative deviation from experimental data is presented in Table 2.9. In general, according to deviations, the models showed good predictive capability. These results reinforce the previous observation of Larsen et al. [2] that the UNIFAC-Lyngby model is accurate for the prediction of VLE data. Utilization of the groups and temperature-independent interaction parameters suggested by Peres and Macedo [7] increased the accuracy of the prediction. There were probably two reasons for these results: i) the introduction of the two cyclic groups in the molecule decomposition and ii) the modification of the interaction parameters of the hydroxyl group of the cyclic structure of both molecules (by the introduction of the OH_{ring} group). In addition, it should be pointed out that, despite the temperature-independence of the interaction parameters, the temperature range evaluated was not significant for observation of high deviations in the predicted boiling point from experimental data.

Table 2.9
Global mean-relative deviation $\sigma(\%)$ of predicted data from experimental data (in Kelvin): (id.) ideal assumption, (A) aliphatic groups [2], (B) Peres and Macedo [9] and (C) Peres and Macedo [7].

System	id.	(A)	(B)	(C)
D-Glucose + water	0.19	0.25	0.13	0.08
D-Fructose + water	0.28	0.33	0.15	0.13
$\sigma(\%)$ =	0.23	0.29	0.14	0.10

As previously observed, the utilization of the aliphatic groups (CH_2, CH, C, OH, H_2O and CH–O) and their interaction parameters, obtained from Larsen et al. [2] database was not efficient for prediction of boiling point data, despite the use of temperature-dependent parameters. In fact, D-glucose and D-fructose are cyclic molecules in aqueous solutions, whose interactions are extensively different than the aliphatic conformations because it is known that the bond energy is a function of the molecule geometry [21, 17]. Moreover, the deviations also showed that the accuracy of the classical approach is slightly worse than the ideal assumption. This suggests that the cyclic conformation is suitable for prediction of the boiling point as well as the precision of the molecular group decomposition.

Since at lower concentrations the boiling point data predicted by ideal assumption is quite the same as the data predicted by the other group-contribution approaches, it could be stated that D-glucose + water and D-fructose + water mixtures with soluble solutes concentration up to approximately 30 % by mass can be considered as ideal solutions (γ_i =

1). This result is very interesting for the design and operation of evaporators that work with low concentrations because the greatest problem in the resolution of the boiling point calculation algorithm is the prediction of the activity coefficient. If this coefficient is set up to be unity, vapor pressure of the pure water will be the only temperature-dependent parameter, and thus, the iteration procedure is facilitated. This observation is not valid for higher concentrations.

The good agreement of the Peres and Macedo [9] approach, that determined structural and interaction parameters considering the sugar molecules as a unique group, was not expected. In general, molecular models do not present good accuracy in extrapolated observations because they are modeled from particular pressure and temperature data. However, taking into account that in this work the temperature and pressure ranges were relatively small, the model could be extrapolated with success.

In addition, despite the formation of volatile compounds when sugar solutions are submitted to heat-treatment [21], this work considered that there is only water in the vapor phase. In fact, some authors found that the concentration of volatile compounds in the vapor phase and the hydrolysis of sugars in the liquid phase are totally negligible for determination of the boiling point of aqueous sugars and fruit juice solutions in the evaluated ranges of pressure and temperature [16, 22]. Thus, these facts did not influence the deviations.

2.3.3 Dühring's rule

Several authors have represented boiling point data of solutions with Dühring's rule [23]. Holven [24], Varshney and Barhate [25], Telis-Romero et al. [26, 27] and Gabas et al. [28] have shown that this rule is applicable to fruit juices and aqueous sugar solutions with a considerable degree of accuracy. The Dühring's rule consists of relating the boiling temperature of a solution with the boiling temperature of the solvent at the same pressure. Therefore, at a constant concentration, this relation takes the form of Eq. (2.15).

$$T_A = m_0 + m_1 T_{A0} \qquad (2.15)$$

where T_A and T_{A0} are, respectively, the boiling temperature of sugar + water solution and water at the same pressure, calculated by Antoine's equation (Eq. 2.11). In this work, parameters m_0 and m_1 were determined by linear regression for each concentration (Table 2.10). The good accuracy of the Dühring's rule can be seen in Fig. (2.5) and (2.6) that present the boiling point of D-glucose + water and D-fructose + water solutions at different soluble solute concentrations as a function of the boiling point of water. Because the boiling temperature is concentration-dependent and the correlation coefficient was good, utilization of the mean-soluble solute concentrations among the pressures was possible and the variation of the concentration during each experiment could be neglected.

Table 2.10
Parameters of Eq. (2.15) for monossacharide (1) + water (2) mixtures at different mean-soluble solute concentrations among the pressures ($\overline{w}_1$ in % by mass).

D-glucose (1) + water (2)				D-fructose (1) + water (2)			
$\overline{w}_1$	m_1	m_0 (ºC)	r^2	$\overline{w}_1$	m_1	m_0 (ºC)	r^2
10.3	1.007	0.113	0.999	10.3	1.019	0.756	0.999
20.3	1.015	0.172	0.999	20.9	1.011	0.589	0.999
28.6	1.018	0.160	0.999	30.9	1.007	1.380	0.999
39.4	1.021	0.149	0.999	41.0	1.014	1.262	0.999
49.4	1.017	1.589	0.999	51.6	1.021	1.822	0.999
60.6	1.022	3.076	0.999	61.1	1.027	2.986	0.999

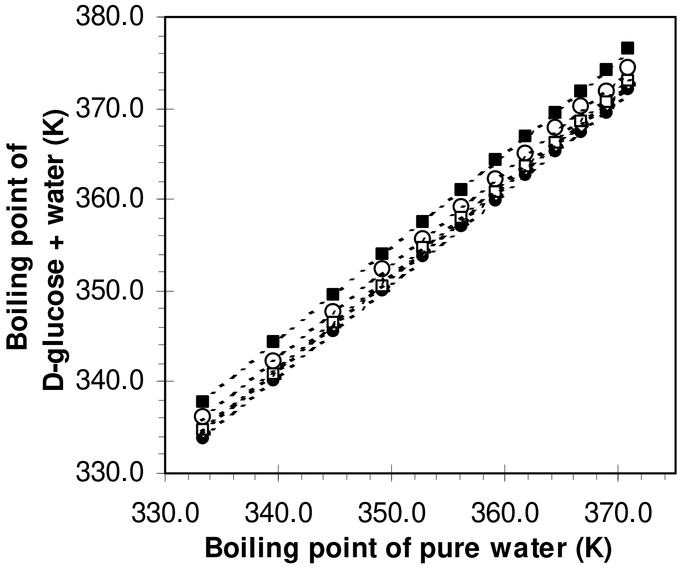

Fig. 2.5. Boiling point of D-glucose + water solutions at different soluble solute contents as a function of the boiling point of pure water. Mean-soluble solute concentrations (% by mass): (●)10.3, (◇)20.3, (□) 28.6, (▲) 39.4, (○) 49.4, (■) 60.6 and (---) is the linear regression.

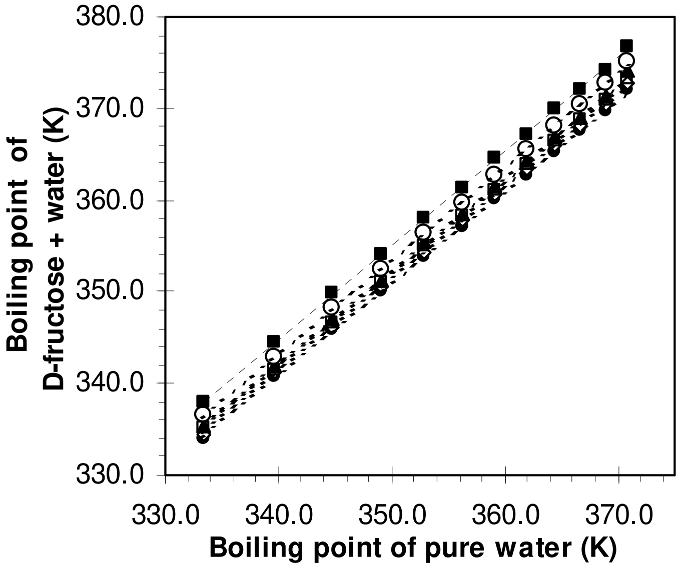

Fig. 2.6. Boiling point of D-fructose + water solutions at different soluble solute contents as a function of the boiling point of pure water. Mean-soluble solute concentrations (% by mass): (●)10.3, (◇)20.9, (□) 30.9, (▲) 41.0, (○) 51.6, (■) 61.1 and (---) is the linear regression.

Figures (2.7) and (2.8) present the rise in boiling point of D-glucose + water and D-fructose + water solutions ($T_A - T_{A0}$) as a function of the boiling point of pure water at different soluble solute contents. For better representation, outliers in experimental data were excluded from the analysis. It was observed that the rise in boiling point is insensitive to pressure, because the slopes of the lines (boiling point rise *versus* boiling point of pure water) are almost negligible (if it was considered that the precision of the temperature sensor is 0.1 K). However, slight deviations on the slopes began to occur at higher concentrations (above 40 % by mass, approximately). At this range of concentration, the rise in boiling point of aqueous sugar solutions is not only concentration-dependent and it is accurate to account also for pressure dependence on the design of heat and mass transport operations.

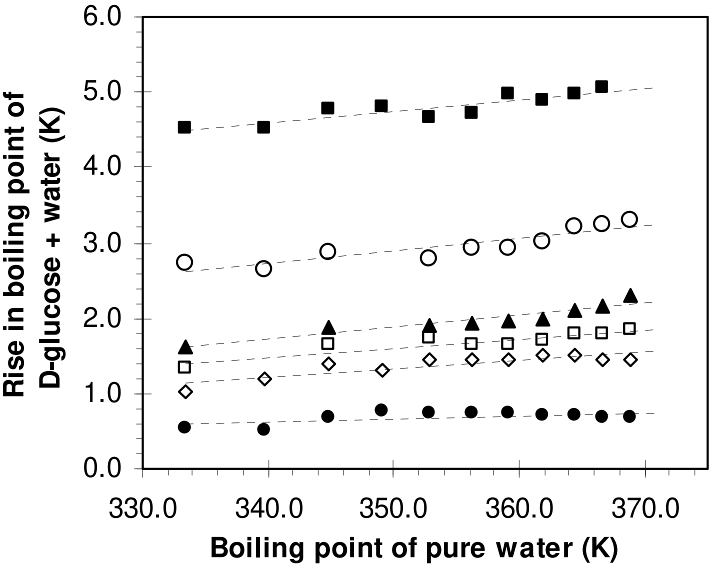

Fig. 2.7. Rise in boiling point of D-glucose + water solutions at different soluble solute contents as a function of the boiling point of pure water. Mean-soluble solute concentrations (% by mass): (●)10.3, (◇)20.3, (□) 28.6, (▲) 39.4, (○) 49.4, (■) 60.6.

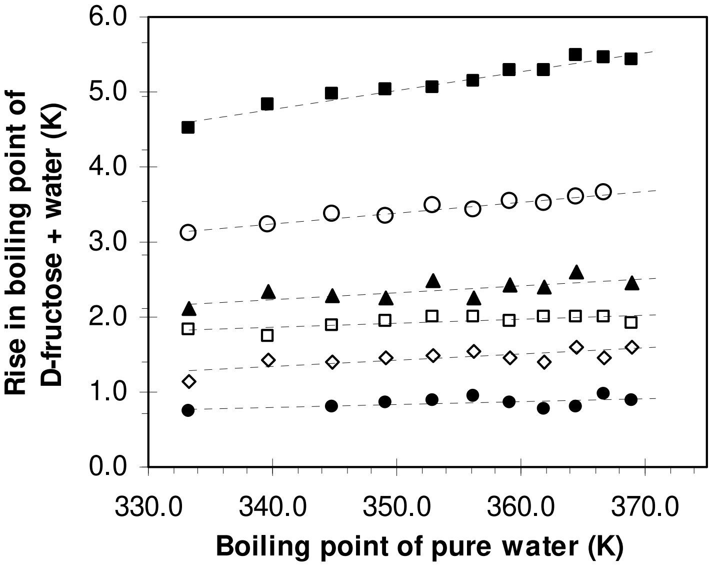

Fig. 2.8. Rise in boiling point of D-fructose + water solutions at different soluble solute contents as a function of the boiling point of pure water. Mean-soluble solute concentrations (% by mass): (●)10.3, (◇)20.9, (□) 30.9, (▲) 41.0, (○) 51.6, (■) 61.1.

2.3.4 Activity coefficients

Tables 2.11 and 2.12 present the activity coefficients of D-glucose, D-fructose and water of the D-glucose + water and D-fructose + water mixtures, from the experimental range of concentration and pressure, calculated by the UNIFAC-Lyngby model with the groups proposed by Peres and Macedo [7], knowing that this approach obtained better accuracy for prediction of the boiling point of aqueous sugar solutions.

Table 2.11

Activity coefficients γ_i of D-glucose(1) + water (2) mixtures calculated by UNIFAC-Lyngby with groups proposed by Peres and Macedo [7]. Mean-soluble solute concentrations $\bar{w}_1$ in % by mass.

$\bar{w}_1$	γ_1	γ_2	γ_1	γ_2	γ_1	γ_2	γ_1	γ_2
	20.0 kPa		26.7 kPa		33.3 kPa		40.0 kPa	
10.3	0.0760	0.9996	0.0804	0.9996	0.0840	0.9996	0.0870	0.9996
20.3	0.0833	0.9980	0.0880	0.9980	0.0917	0.9980	0.0950	0.9980
28.6	0.0905	0.9954	0.0962	0.9952	0.1006	0.9951	0.1042	0.9951
39.4	0.1044	0.9884	0.1100	0.9885	0.1149	0.9885	0.1191	0.9884
49.4	0.1233	0.9760	0.1296	0.9763	0.1347	0.9765	0.1393	0.9766
60.6	0.1569	0.9490	0.1644	0.9497	0.1709	0.9498	0.1760	0.9503
	46.7 kPa		53.3 kPa		60.0 kPa		66.7 kPa	
10.3	0.0896	0.9996	0.0920	0.9996	0.0941	0.9996	0.0961	0.9996
20.3	0.0978	0.9980	0.1003	0.9981	0.1027	0.9980	0.1047	0.9981
28.6	0.1071	0.9952	0.1096	0.9953	0.1123	0.9952	0.1137	0.9955
39.4	0.1222	0.9886	0.1250	0.9887	0.1279	0.9887	0.1305	0.9887
49.4	0.1430	0.9767	0.1466	0.9767	0.1499	0.9767	0.1528	0.9767
60.6	0.1804	0.9506	0.1847	0.9506	0.1882	0.9509	0.1914	0.9512
	73.3 kPa		80.0 kPa		86.7 kPa		93.6 kPa	
10.3	0.0979	0.9996	0.0995	0.9996	0.1011	0.9996	0.1027	0.9996
20.3	0.1067	0.9980	0.1085	0.9980	0.1102	0.9980	0.1119	0.9980
28.6	0.1154	0.9956	0.1169	0.9958	0.1195	0.9955	0.1221	0.9952
39.4	0.1327	0.9887	0.1348	0.9888	0.1367	0.9888	0.1386	0.9889
49.4	0.1553	0.9768	0.1577	0.9769	0.1598	0.9769	0.1619	0.9770
60.6	0.1943	0.9514	0.1979	0.9510	0.2009	0.9509	0.2038	0.9507

Table 2.12

Activity coefficients γ_i of D-fructose (1) + water (2) mixtures calculated by UNIFAC-Lyngby with groups proposed by Peres and Macedo [7]. Mean-soluble solute concentrations $\bar{w}_1$ in % by mass.

$\bar{w}_1$	γ_1	γ_2	γ_1	γ_2	γ_1	γ_2	γ_1	γ_2
	20.0 kPa		26.7 kPa		33.3 kPa		40.0 kPa	
10.3	0.0196	0.9994	0.0214	0.9994	0.0228	0.9994	0.0241	0.9994
20.9	0.0225	0.9969	0.0245	0.9969	0.0261	0.9969	0.0275	0.9969
30.9	0.0266	0.9914	0.0287	0.9915	0.0305	0.9918	0.0321	0.9918
41.0	0.0323	0.9809	0.0350	0.9811	0.0371	0.9813	0.0390	0.9815
51.6	0.0417	0.9608	0.0451	0.9610	0.0479	0.9612	0.0503	0.9612
61.1	0.0571	0.9253	0.0612	0.9263	0.0649	0.9265	0.0678	0.9271
	46.7 kPa		53.3 kPa		60.0 kPa		66.7 kPa	
10.3	0.0251	0.9994	0.0262	0.9994	0.0271	0.9994	0.0279	0.9994
20.9	0.0288	0.9969	0.0299	0.9969	0.0310	0.9970	0.0319	0.9970
30.9	0.0336	0.9918	0.0349	0.9918	0.0360	0.9919	0.0372	0.9918
41.0	0.0407	0.9816	0.0423	0.9815	0.0438	0.9815	0.0450	0.9815
51.6	0.0525	0.9612	0.0544	0.9615	0.0559	0.9620	0.0574	0.9622
61.1	0.0707	0.9272	0.0730	0.9276	0.0751	0.9280	0.0768	0.9289
	73.3 kPa		80.0 kPa		86.7 kPa		93.6 kPa	
10.3	0.0287	0.9994	0.0295	0.9994	0.0301	0.9994	0.0308	0.9994
20.9	0.0328	0.9970	0.0336	0.9970	0.0344	0.9970	0.0352	0.9970
30.9	0.0383	0.9917	0.0393	0.9917	0.0401	0.9917	0.0410	0.9918
41.0	0.0462	0.9816	0.0471	0.9820	0.0480	0.9822	0.0494	0.9817
51.6	0.0590	0.9621	0.0606	0.9617	0.0620	0.9616	0.0634	0.9615
61.1	0.0786	0.9292	0.0800	0.9299	0.0810	0.9311	0.0836	0.9296

Once the symmetrical convention was used for activity coefficient calculation, i.e., the standard state of each solution component *i* is considered as pure liquid *i* at the temperature of the solution ($\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$, for each *i*), it was possible to state that all solution components presented a negative deviation from the ideal ($\gamma_i < 1$). This fact shows that the partial pressure of the water is less than the corresponding ideal solution as well as the Gibbs free energy (*G*). The decrease of *G* reveals that the aqueous sugar solution becomes more stable than the ideal solution. The greater stability and decreasing of the partial pressure of water lead to a smaller escape tendency by vaporizing, increasing the boiling point. The increase in the sugar concentration also decreased the activity coefficient of water (Tables 2.11 and 2.12) , i.e., decreased the tendency of water vaporization and the small activity coefficients of sugars agree with the lack of volatility of these compounds. Moreover, the activity coefficient data showed that D-fructose in the solution presented a slightly superior deviation from ideality than D-glucose. This agrees with the experimental boiling point data and the previous observation regarding the molecular conformation of D-fructose and D-glucose.

As observed, the behavior of the boiling point as a function of concentration is close to an exponential function, because at higher sugar concentration a slight increase of the amount of solute led to a great increase in boiling point. The same behavior can be observed in the effect of pressure on the boiling point rise, as shown in the Dühring's rule evaluation (Figures 2.7 and 2.8). Thus, the increasing of the concentration and pressure (for higher concentrations) elevates the heat necessary for vaporization processes and also leads to the decrease of *G*, as observed. If it was stated that the free Gibbs energy is a parameter of the non-ideality evaluation and this property is null for an ideal solution, it can again be stated that the solution deviated from ideality as concentration and pressure (for higher concentrations) increased in the evaporation process. In fact, the energetic interactions among the molecules in a solution lead to a deviation from the ideal which is dependent on the nature of the species, concentration, temperature and pressure [11]. At low concentrations, solvent–solute interactions are predominant but, as concentration rises, solute–solute interactions became more relevant. However, since the UNIFAC model was not developed to take into account the effect of some chemical bonds widely found in aqueous solutions, such as the hydrogen bond, the deviations are expected to grow with the solute concentration.

2.4 Conclusions

The modified group contribution UNIFAC model proposed by Larsen et al. [2] was used in this study because of its robustness with regards to temperature deviation. It presented good accuracy for VLE prediction. The groups suggested by Peres and Macedo [7] were checked according to accuracy and obtained excellent agreement for monossacharide + water mixtures at different concentrations and pressures. It was observed that the particular cyclic conformation of sugar is highly relevant for the boiling point data prediction. The observations and experimental results could be successfully checked by the thermodynamic approach and Dühring's rule. This work therefore improves the experimental boiling point database of literature, as well as the activity coefficient data calculated by the UNIFAC-Lyngby model.

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CAPÍTULO 3

pH of aqueous polycarboxylic acid solutions: Experimental determination and modeling with group contribution method

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pH of aqueous polycarboxylic acid solutions: Experimental determination and modeling with group contribution method

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Abstract

Optimization of food and biochemical processes requires the knowledge of reliable thermophysical properties. Some of these properties, such as pH, are evaluated by chemical equilibrium analysis of solution species. The pH is an important parameter of food processes because it establishes the sensorial and microbiological attributes of a food. Fruit juices can be represented by model mixtures composed by sugars, polycarboxylic acids, proteins, salts, fiber and also fatty acids. Some of these aqueous solutions present weak electrolytes, whose concentration of the ionic species resulted from dissociation protonation depends on the equilibrium conditions. The aim of this work was to measure and modeling the pH of aqueous polycarboxylic acid solutions at different temperatures and concentrations. The UNIFAC-Lyngby model and the modified Debye-Hückel term were used for predicting the asymmetrical activity coefficient of the ionic and nonionic species in the mixture. A nonlinear system of equations based on electrolyte mass balances, electroneutrality assumption and dissociation constants of the polycarboxylic acids was solved by a numerical method implemented in MATLAB 7.0 for calculation of concentrations of each specie in the mixture. It was observed that the behavior of the pH and the individual activity coefficients of species are dependent on temperature, concentration of solutes, ionic charge and kind of acid. The measured and calculated data using the UNIFAC-Lyngby model + modified Debye-Hückel term showed a good agreement. As expected, the "short-range" term of the UNIFAC-Lyngby model plays an important role at higher solute concentration in the solution. On the other hand, at lower concentrations, the modified Debye-Hückel term is more appropriate accounting for the electrostatic interactions ("long-range" interactions).

Keywords: UNIFAC, Debye-Hückel, polycarboxylic acids, hydrochloric acid, pH

3.1 Introduction

Thermodynamic modeling based on excess Gibbs energy models or equations of state have been used on food chemistry for several years to describe and predict the behavior of food systems at several conditions of pressure and temperature. It can be seen in literature that the group contribution methods are a powerful tool for analysis of phase equilibrium in food systems [1]. Among the predictive models, the UNIFAC method [2] is widely applied to the prediction of the phase equilibrium of nonideal nonelectrolyte systems. To calculate the activity coefficients, the UNIFAC model takes into account differences in size and shape of the components in the solution and the energetic interactions among the functional groups in the mixture. Larsen et al. [3] modified the

Staverman-Guggenheim combinatorial term of the UNIFAC model and introduced the modified ($r^{2/3}$) Flory-Huggins combinatorial term. They verified that the modified UNIFAC gives in general predictions of liquid-liquid equilibrium (LLE) of the same quality as the original UNIFAC with LLE-based parameters but provides a better agreement with regard to experimental and calculated data at other temperatures. The UNIFAC-Lyngby model is presented below, from Eqs (3.1) to (3.10).

$$ln\ \gamma_i = ln\ \gamma_i^c + ln\gamma_i^r \tag{3.1}$$

$$\ln \gamma_i^c = \ln \frac{\varpi_i}{x_i} + 1 - \frac{\varpi_i}{x_i} \tag{3.2}$$

$$\ln \gamma_i^r = \sum_{k=1}^{n} v_k^i \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \tag{3.3}$$

$$\varpi_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \tag{3.4}$$

$$r_i = \sum_{k=1}^{n} v_k^{(i)} R_k \tag{3.5}$$

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_{m=1}^{n} \Psi_m \tau_{mk} \right) - \sum_{i=1}^{n} \frac{\Psi_i \tau_{ki}}{\sum_{j=1}^{n} \Psi_j \tau_{ji}} \right] \tag{3.6}$$

$$\Psi_m = \frac{Q_m X_m}{\sum_{p=1}^{n} Q_p X_p} \tag{3.7}$$

$$X_m = \frac{\sum_{j=1}^{n} v_m^{(j)} x_j}{\sum_{j=1}^{n} \sum_{p=1}^{n} v_p^{(j)} x_j} \tag{3.8}$$

$$\tau_{mk} = \exp\left(\frac{-a_{mk}}{T}\right) \quad (3.9)$$

$$a_{mk} = a_{mk,1} + a_{mk,2}\,(T-T_0) + a_{mk,3}\,(\,T\,ln(T_0/T) + T - T_0) \quad (3.10)$$

where γ_i is the symmetrical activity coefficient of the molecule i, γ_i^c is the combinatorial term and γ_i^r is the residual term for the activity coefficient, x_i is the molar fraction, ω_i is the volume fraction of the molecule i, r_i is the molecular volume parameter, ν_{ki} is the number of groups of type k in molecule i, Γ_k is the activity coefficient of group k at mixture composition and Γ_k^i is the activity coefficient of group k at a group composition corresponding to the pure component i, Ψ_i is the surface area fraction of component i in mixture, X_m is the group mole fraction of group m and τ_{mk} is the Boltzmann factor. The structural parameters R_k and Q_k for the groups and the temperature-dependent group-interaction parameters a_{mk} are obtained from properties data tables [4]. T is the temperature (K) and T_0 is the reference temperature (298.15 K).

Aqueous-based food processes (such as membrane separations, pH-controlled applications or bioprocesses) and food mixtures (such as fruit juices, dairy food or protein suplements) have emerged interest in predictive models that account for the presence of electrolytes in solutions. Aqueous electrolyte solutions contain dissociated species whose ionic charges cause electrostatic interactions which must be taken into account for calculation of the thermodynamical properties. Debye and Hückel [5], probably the most reported authors in the area, derived from the variation of the free Gibbs energy between the ideal and nonideal solution, an equation for calculating activity coefficients of diluted electrolyte solutions. However, because complex mixtures have both, electrolytes and nonelectrolytes, the activity coefficients of the species in the mixture should be calculated by a sum of two terms, one related to electrostatic interactions, called as long-range forces

(LR) and other related to other intermolecular interactions, called short-range forces (SR). Achard et al. [6] used the UNIFAC-Lyngby model for calculating SR forces contributions and the modified Debye-Hückel term proposed by Pitzer [7] for LR forces contributions for prediction of γ_i for those solutions (Eq. 3.11). However, because Debye-Hückel term modified by Pitzer [7] (Eq. 3.12) uses the asymmetrical convention, i.e., the standard state of each solution component *i* is taken as the infinitely diluted solution of *i* at the temperature of the solution ($\gamma_i \rightarrow 1$ as $x_i \rightarrow 0$, for each *i*) it is necessary to standardize the UNIFAC-Lyngby (Eq. 3.13) as follows:

$$\ln \gamma_i^{*} = \ln \gamma_i^{*SR} + \ln \gamma_i^{*LR} \tag{3.11}$$

$$\ln \gamma_i{}^{*LR} = -\left(\frac{1000}{M_s}\right)^{0.5} A_{\Phi}\left[\left(\frac{2z_i^2}{17.1}\right)\ln\left(1+17.1 I_x^{0.5}\right)+\frac{\left(z_i^2 I_x^{0.5}-2I_x^{1.5}\right)}{\left(1+17.1 I_x^{0.5}\right)}\right] \tag{3.12}$$

$$\ln \gamma_i{}^{*SR} = \ln \gamma_i^{SR} - \ln\left(\lim_{x_i \rightarrow 0} \gamma_i^{SR}\right) \tag{3.13}$$

where γ_i* is the asymmetrical activity coefficient of specie *i*, $\gamma_i{}^{*LR}$ is the long-range term of the asymmetrical activity coefficient of species *i,* $\gamma_i{}^{*SR}$ is the short-range term of the asymmetrical activity coefficient of species *i,* γ_i^{SR} is the SR term in the symmetrical convention, M_s is the molar mass of water, A_{Φ} is the Debye-Hückel parameter ($A_{\Phi} = 1.40060814 \cdot 10^{6}\, d_s^{0.5}\, (D_s T)^{-1.5}$), d_s is the density of the solvent (g cm^{-3}), D_s is the dielectrical constant of the solvent ($D_s = -31.61 + 32733.43\, T^{1}$), T is temperature in Kelvin, z_i is the ion charge and I_x is the ionic strength ($I_x = (½)\, \Sigma x_i z_i^2$) [6].

Several authors have used the mentioned approach for the prediction of the phase equilibrium and thermodynamic properties of electrolyte mixtures. Achard et al. [6] validated the proposed approach by calculation of pH of binary aqueous organic and inorganic acids solutions, food and fermentation broth model mixtures (containing sugar, salts and organic acids) at 25 ºC and obtained good agreement between calculated and experimental data for low concentrated solutions. Gros and Dussap [8] estimated equilibrium properties in model mixtures of milk, buffer solutions and energy drinks and did not obtain good agreement for more complex systems. Maffia and Meirelles [9] used the same UNIFAC-Lyngby and the Debye-Hückel term proposed by Pitzer [7] for accurately prediction of the water activity and pH of aqueous polycarboxylic acid systems and fruit juice models at 25 ºC. Kuramoshi et al. [10] proposed the utilization of the same approach for representation of the activity coefficients of biochemicals and obtained satisfatory agreement for binary systems. Ninni and Meirelles [11] used the model for the accurate prediction of the water activity, pH and density of aqueous and nonaqueous amino acids systems at 25 ºC.

Although chemical equilibrium of polycarboxylic acids has already been studied with the mentioned model from Achard et al. [6], this work aimed to evaluate the behavior of the activity coefficient of aqueous polycarboxylic acids solutions under different temperature conditions and at the concentration range found in concentrated and *in natura* fruit juices. Moreover, the behavior of the UNIFAC-Lyngby model and the Debye-Hückel term modified by Pitzer [7] was evaluated accounting for the significance of the long-range and short-range interactions in the systems. In contrast to prior works the present study takes into account a more comprehensive data bank on pH and activity coefficients of polycarboxylic acids solutions and models these properties considering the effect of temperature on the partial dissociation of weak electrolytes.

3.2 Material and Methods

Samples of the polycarboxylic acids were supplied by Merck (USA) with purity greater than 99 % by mass. Binary solutions (acid + water) were prepared gravimetrically with deionized water (Millipore, USA) using an analytical balance (Precisa Instruments, Switzerland) with precision of 1 x 10^{-4} g. The water content in the solid polycarboxylic acid samples was determined by Karl Fisher titration with a Metrohm Titrino 701 apparatus (Metrohm, Switzerland) and the concentration of the binary systems was calculated.

The experimental pH data of the binary aqueous mixtures with citric acid, malic acid, malonic acid, oxalic acid, succinic acid and tartaric acid were obtained with a KCl electrode with a 0.001 precision, in pH units, Metrohm Titrando 808 apparatus (Metrohm, Switzerland). The device was calibrated with buffer solutions (pH 4 and 7), supplied by Synth (Brazil). The electrode was maintained in a 3 mol L^{-1} KCl solution and calibrated with the appropriate buffers after a regular period of measurements for its stabilization. The measurements were conducted in a temperature range from 278.15 to 323.15 K and in a concentration range of the polycarboxylic acids between 1 to 20 % by mass, approximately. For this purpose, 50 mL of each binary mixture were put in a 50 mL covered jacked glass cell with magnetic stirring (Marconi, Brazil). The temperature was controlled using a thermostated water bath (VT2 Anton Paar, Austria) and monitored by a 0.1 K precision calibrated digital thermometer inside the aqueous mixtures. Measurements were taken after stabilization of the desired temperature and were made in triplicate with a reproducibility of ± 0.001 pH units.

Prediction of pH values (Eq. 3.14) was carried out by calculation of the asymmetrical activity coefficient γ^* and concentration of ions H^+.

$$pH = -\log(\gamma^*_{H^+} c_{H^+}) = -\log\left(\frac{\gamma^*_{H^+} x_{H^+}}{v_w}\right) \qquad (3.14)$$

where c_{H+} and x_{H+} stand for molar concentration and molar fraction of ions H^+, respectively, and v_w is the molar volume of water (L mol^{-1}). Because of the dissociation phenomena, the solution was treated like a multicomponent system, composed by 2 nonionic species (nondissociated acid and water molecules), 2 ionic species for dicarboxylic acids or 3 ionic species for tricarboxylic acids, obtained from the acid dissociation and 2 ionic species from water dissociation (H^+ and OH^-).

The asymmetrical activity coefficient of ion H^+ was calculated by Eq. (3.11). Table 3.1 presents the chemical structure of the polycarboxylic acids used in this work and their ions. Table 3.2 shows the UNIFAC structural and interaction parameters of nonionic [3] and ionic species [6]. The interaction parameter of the ion COO^- was taken from polycarboxylic acid database fitted by Velezmoro and Meirelles [12]. Also, because of short-range forces include solvation phenomena, the hydration number *Nh* of the ions were considered. The *Nh* corresponds to the number of water molecules assumed to be chemically bound to the charged species. Thus, the mole fractions x_i^H (Eqs. 3.15 and 3.16) and the structural parameters R_k^H of hydrated species (Eq. 3.17) were used for calculation of $\gamma_i^{SR,H}$ (short-range term of activity coefficient using hydrated species). Thus, the γ_i^{SR} was calculated by equation 3.18. The *Nh* of ion H^+ was set to 2.959 and the others were set to zero [6].

$$x_1^H = \frac{x_1 - \sum_{k=2} Nh_k x_k}{1 - \sum_{k=2} Nh_k x_k} \tag{3.15}$$

$$x_i^H = \frac{x_i}{1 - \sum_{k=2} Nh_k x_k} \tag{3.16}$$

$$R_k^H = R_k + Nh_k R_1 \tag{3.17}$$

$$\gamma_i^{SR} = \frac{\gamma_i^{SR,H} x_i^H}{x_i (\gamma_1^{SR,H} x_1^H)^{-Nh_i}} \tag{3.18}$$

where the subscribed *1* refer to water, Nh_k represents the infinite dilution hydration number of *k* and x_k is the mole fraction of *k*.

Table 3.1
UNIFAC groups of polycarboxylic acids and their ions.

Polycarboxylic acid	Ionic specie	CH_2	CH	C	OH	COOH	COO^-
Citric acid		2	0	1	1	3	0
	$H_2Citric^-$	2	0	1	1	2	1
	$HCitric^{2-}$	2	0	1	1	1	2
	$Citric^{3-}$	2	0	1	1	0	3
Malic acid		1	1	0	1	2	0
	$HMalic^-$	1	1	0	1	1	1
	$Malic^{2-}$	1	1	0	1	0	2
Malonic acid		1	0	0	0	2	0
	$HMalonic^-$	1	0	0	0	1	1
	$Malonic^{2-}$	1	0	0	0	0	2
Oxalic acid		0	0	0	0	2	0
	$HOxalic^-$	0	0	0	0	1	1
	$Oxalic^{2-}$	0	0	0	0	0	2
Succinic acid		2	0	0	0	2	0
	$HSuccinic^-$	2	0	0	0	1	1
	$Succinic^{2-}$	2	0	0	0	0	2
Tartaric acid		0	2	0	2	2	0
	$HTartaric^-$	0	2	0	2	1	1
	$Tartaric^{2-}$	0	2	0	2	0	2

Table 3.2
UNIFAC structural and interaction parameters

Structural Parameters			Interaction parameters (each row gives one coefficient of Eq. 3.10: $a_{mk,1}$, $a_{mk,2}$ e $a_{mk,3}$)								
					k						
Group	R_k	Q_k	*Ref.*	*m*	CH_2	OH	H_2O	COOH	COO^-	H^+	OH^-
CH_2	0.6744	0.5400			0.0	972.8	1857.0	664.1	-2500.0	-1150.0	0.0
CH	0.4469	0.2280	[3]	CH_2	0.0	0.2687	-3.322	1.317	0.0	0.0	0.0
C	0.2195	0.0000			0.0	8.773	-9.000	-4.904	0.0	0.0	0.0
					637.5	0.0	155.6	-1184.9	-2500.0	-1650.0	-3450.0
OH	1.0000	1.2000	[3]	OH	-5.832	0.0	0.3761	4.847	0.0	0.0	0.0
					-0.8703	0.0	-9.000	0.0	0.0	0.0	0.0
					410.7	-47.15	0.0	-1054.0	-2500.0	-2356.24	-3802.46
H_2O	0.9200	1.4000	[3]	H_2O	2.868	-0.4947	0.0	2.446	0.0	0.0	0.0
					9.000	8.650	0.0	0.0	0.0	0.0	0.0
					171.5	1997.6	1616.0	0.0	-2500.0	-2500.0	-2500.0
COOH	1.3013	1.2240	[3]	COOH	-1.463	-6.714	-5.66	0.0	0.0	0.0	0.0
					0.6759	0.0	0.0	0.0	0.0	0.0	0.0
					-746.3	497.3	700.0	622.18	0.0	-2500.0	0.0
COO^-	1.3013	1.2240	[12]	COO^-	0.0	0.0	0.0	0.0	0.0	0.0	0.0
					0.0	0.0	0.0	0.0	0.0	0.0	0.0
					603.7	1347.3	843.76	622.18	-2500.0	0.0	-2500.0
H^+	0.4661	0.6018	[6]	H^+	0.0	0.0	0.0	0.0	0.0	0.0	0.0
					0.0	0.0	0.0	0.0	0.0	0.0	0.0
					1753.7	452.7	-602.46	622.18	0.0	-2500.0	0.0
OH^-	0.3912	0.5354	[6]	OH^-	0.0	0.0	0.0	0.0	0.0	0.0	0.0
					0.0	0.0	0.0	0.0	0.0	0.0	0.0

The concentration of ion H^+ was obtained from the evaluation of the chemical equilibrium equations (Eq. 3.19 to 3.22), the mass balance of dissociated and nondissociated species (Eqs. 3.23 and 3.24), the electroneutrality condition (Eq. 3.25) and the dissociation equilibrium constants (Eqs. 3.26 to 3.28). The following equations show the chemical equilibrium of a tricarboxylic acid (H_3X) + water solution. For an aqueous dicarboxylic acid solution the third dissociation should be neglected.

$$H_3X \leftrightarrow H_2X^- + H^+ \qquad K_1 \qquad (3.19)$$

$$H_2X^- \leftrightarrow HX^{--} + H^+ \qquad K_2 \qquad (3.20)$$

$$HX^{--} \leftrightarrow X^{---} + H^+ \qquad K_3 \qquad (3.21)$$

$$H_2O \leftrightarrow OH^- + H^+ \qquad K_{water} \qquad (3.22)$$

$$c_{H_2X,o} = c_{H_2X,f} + c_{H_2X^-} + c_{HX^{--}} + c_{X^{---}} \qquad (3.23)$$

$$c_{H_2O,o} = c_{H_2O,f} + c_{OH^-} \qquad (3.24)$$

$$c_{H^+} = c_{OH^-} + c_{H_2X^-} + 2c_{HX^{--}} + 3c_{X^{---}} \qquad (3.25)$$

$$K_1 = \frac{(\gamma^*_{H^+} c_{H^+})(\gamma^*_{H_2X^-} c_{H_2X^-})}{(\gamma^*_{H_3X} c_{H_3X})} \frac{\upsilon_m}{\upsilon_w} \qquad (3.26)$$

$$K_2 = \frac{(\gamma^*_{H^+} c_{H^+})(\gamma^*_{HX^{--}} c_{HX^{--}})}{(\gamma^*_{H_2X^-} c_{H_2X^-})} \frac{\upsilon_m}{\upsilon_w} \qquad (3.27)$$

$$K_3 = \frac{(\gamma^*_{H^+} c_{H^+})(\gamma^*_{X^{---}} c_{X^{---}})}{(\gamma^*_{HX^{--}} c_{HX^{--}})} \frac{\upsilon_m}{\upsilon_w} \qquad (3.28)$$

where c is the molar concentration (mol L^{-1}) of the subscribed specie, the subscripts o and f denote initial and final concentrations of species, respectively, K_i is the dissociation constant of the *i-th* equation of the chemical equilibrium and v_m is the molar volume of the mixture (L mol^{-1}). Moreover, since chemical equilibrium is temperature-dependent (Le

Chatelier principle) [13], it was taken into account the effect of temperature on K_i for the calculation of the concentration of ion H^+ (Table 3.3).

Table 3.3
Dissociation constant of polycarboxylic acid from 278.15 to 323.15 K ($pK_i = -\log K_i$)

Polycarboxylic acid			Temperature (K)									
		Ref.	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15
Citric	pK_1	[14]	3.200	3.176	3.160	3.142	3.128	3.116	3.109	3.099	3.097	3.095
	pK_2	[14]	4.813	4.799	4.782	4.769	4.761	4.753	4.750	4.748	4.752	4.755
	pK_3	[14]	6.386	6.383	6.384	6.388	6.396	6.406	6.423	6.439	6.462	6.484
Malic	pK_1	[15]	3.520	3.494	3.483	3.473	3.459	3.453	3.447	3.445	3.446	3.445
	pK_2	[15]	5.108	5.098	5.096	5.096	5.097	5.100	5.105	5.118	5.133	5.149
Malonic	pK_1	[16]	2.882	2.869	2.857	2.851	2.847	2.849	2.855	2.863	2.876	2.897[a]
	pK_2	[17]	5.665	5.667	5.673	5.683	5.696	5.710	5.730	5.753	5.777	5.803[a]
Oxalic	pK_1	[18]	1.256[a]	1.267[a]	1.277	1.288[a]	1.300	1.310	1.320	1.330	1.340	1.360
	pK_2	[19]	4.207	4.218	4.231	4.247	4.266	4.287	4.312	4.338	4.369	4.399
Succinic	pK_1	[20]	4.263	4.245	4.232	4.218	4.207	4.198	4.191	4.188	4.187	4.186
	pK_2	[21]	5.660	5.649	5.643	5.639	5.635	5.641	5.647	5.654	5.669	5.680
Tartaric	pK_1	[22]	3.095	3.075	3.058	3.044	3.033	3.026	3.021	3.018	3.019	3.021
	pK_2	[22]	4.407	4.391	4.379	4.371	4.367	4.365	4.367	4.372	4.380	4.390

[a] extrapolated data by polinomial fitting with MATLAB 7.0.

Thus, for pH prediction, a nonlinear system of equations was composed by the chemical equilibrium equations (Eqs. 3.19 to 3.28), the UNIFAC-Lyngby model (Eq. 3.1) and the modified Debye-Hückel term proposed by Pitzer [7] (Eq. 3.11). The number of variables of the system of equations was reduced to 2 independent variables for dicarboxylic acids and 3 independent variables for tricarboxylic acids. The variables were the concentration of the ionic species of the polycarboxylic acid. Also, due to the interdependence between c_i and γ_i, the system of equations were solved by an optimization algorithm implemented in MATLAB 7.0 (Fig. 3.1), based on the Sequential Quadratic Programming (SQP) and the Quasi-Newton method (MATLAB function *fmincon*) for calculation of the minimum of an objective function. The objective function was the norm of the absolute deviations N of the calculated K_j^{calc} from literature K_j^{lit}. (Eq. 3.29)

$$N = \sqrt{\sum_j \left(K_j^{lit} - K_j^{calc}\right)^2} \tag{3.29}$$

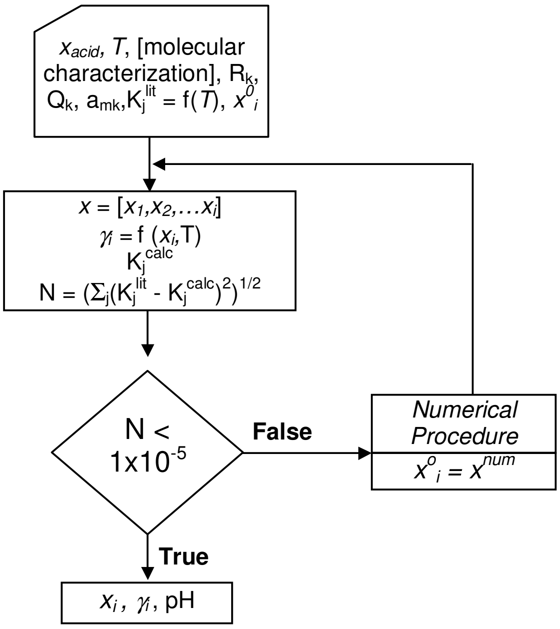


Fig. 3.1. Algorithm for the calculation of pH. x_{acid} is the initial molar fraction of the polycarboxylic acid in the considered binary mixture, T is the experimental temperature of the system, x^0_i is the initial guess for concentration of the i-th independent variable, K_j^{lit} is the literature dissociation constant of the *j-th* equilibrium equation of the *i-th* component of the system, K_j^{calc} is the calculated dissociation constant, x^{num} is a new guess for concentration, given by the numerical procedure.

The first step of the procedure was the recognition of the entrance variables: the initial molar fractions x_i of the binary mixture, the temperature T of the system, the chemical groups of the molecules in the solution and the group structural and interaction parameters, R_k, Q_k and a_{mk} from the database of the aforementioned literature. Initial iteration started with concentration values for the independent variables, sufficiently close to the optimal solution and estimated from the pH of an ideal solution ($pH = -\log\,[c_{H+}]$). Thus, the asymmetrical activity coefficient γ^*_i of the species was calculated to determinate the K_j^{calc} and consequently the objective function. The minimum of the function was found with the SQP and the Quasi-Newton method with values of N less than 10^{-5}.

3.3 Results and discussions

3.3.1 Performance of the methodology

To check the performance of the apparatus, the pH of aqueous solutions of citric acid, malic acid, malonic acid, oxalic acid and tartaric acid in a concentration range from 1 to 20 % by mass at 298.15 K and of aqueous hydrochloric acid mixtures at concentration of 0.01 molal and 0.1 molal (m_{HCL} L_{water}^{-1}) and temperature range from 278.15 to 323.15 K were measured according to the previous methodology and compared with the data from literature [9, 23-25]. The results are presented in Fig. (3.2). Moreover, to check the performance of the algorithm, the predicted pH values of aqueous polycarboxylic acid solutions using the UNIFAC-Lyngby and the Debye-Hückel term modified by Pitzer [7] were compared with the data predicted by Ref. [9] that used the same methodology for γ^* calculation (Fig. 3.3). The agreement between experimental and reported data was good, since the fitted curve (continuous line, determined by linear regression) presented a slight deviation from the diagonal straight line (dashed line). This deviation is approximately less than the precision of the apparatus, since, according to Durst and Bates [26], under carefully controlled experimental conditions, the pH can be measured with an uncertainty of ± 0.005. The predicted pH data are also in agreement with the data from literature, since the fitted curve presented also a slight deviation. This deviation is close to the global-relative deviation presented by Maffia and Meirelles [9] from experimental data (1.31 %) and it is reasonable, taking into account the used algorithm and interaction parameters.

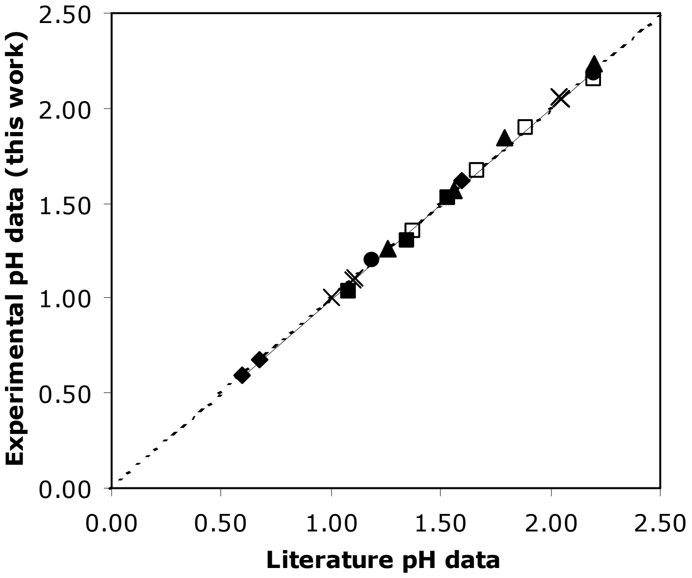


Fig. 3.2. Experimental data (this work) versus data from literature of pH of aqueous solutions containing (■) malonic acid, (●) tartaric acid, (▲) citric acid, (□) malic acid, (◆) oxalic acid. [9, 25] and (×) HCl + water mixtures [23,24]. Dashed line represents the diagonal straight line and the continuous line is the curve fitted with the data (y = 1.0009 x - 0.006, r^2 = 0.9983). Number of observations = 24.

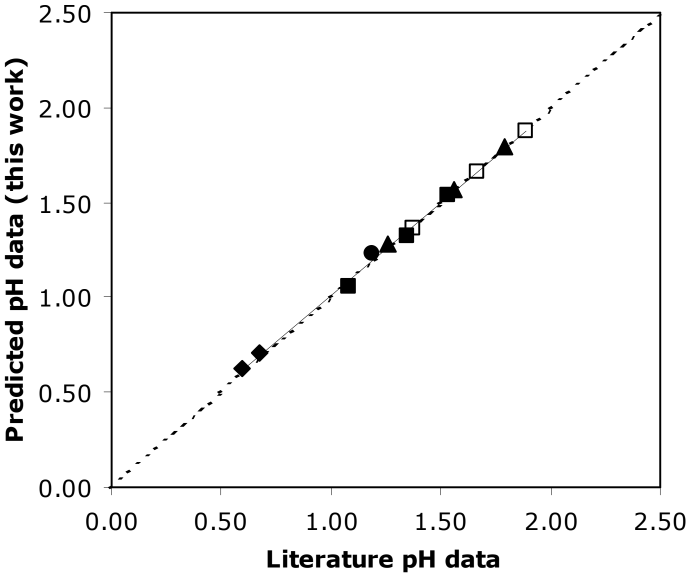


Fig. 3.3. Predicted data (this work) versus predicted data from literature of pH (by UNIFAC-Lyngby + modified Debye-Hückel term proposed by Pitzer [7] of aqueous solutions containing (■) malonic acid, (●) tartaric acid, (▲) citric acid, (□) malic acid, (◆) oxalic acid. [9]. Dashed line represents the diagonal straight line and the continuous line is the curve fitted with the data (y = 0.9772 + 0.049, r^2 = 0.9984). Number of observations = 12.

3.3.2 Experimental and predicted pH data

Tables 3.4 and 3.5 show the experimental pH data of the polycarboxylic acid (1) + water (2) solutions at concentrations up to 20 % by mass and temperatures from 278.15 to 323.15 K as well as a comparison among 3 different approaches for the calculation of the asymmetrical activity coefficients: i) the approach proposed by Achard et al. [6], i.e., prediction of γ^* by UNIFAC-Lyngby model and the modified Debye-Hückel term proposed by Pitzer [7], assuming the existence of short and long-range interactions, ii) using the modified Debye-Hückel term [7] assuming that the deviations from ideality comes from long-range interactions and iii) using the UNIFAC-Lyngby model [3], assuming that the deviation from ideality comes from short-range interactions.

Table 3.4

pH data of polycarboxylic acid (1) + water (2) solutions: (exp.) experimental data, predicted data by (A) UNIFAC-Lyngby + Debye-Hückel term modified by Pitzer [7], (B) modified Debye-Hückel term [7], (C) UNIFAC-Lyngby and (id.) ideal assumption. (w_1 % by mass)

	exp.	(A)	(B)	(C)	id.	exp.	(A)	(B)	(C)	id.	exp.	(A)	(B)	(C)	id.
citric acid (1) + water (2)															
T (K)	w_1 = 1.00 %					w_1 = 2.50 %					w_1 = 5.00 %				
278.15	2.270	2.229	2.240	2.230	2.211	2.040	2.006	2.033	2.007	2.012	1.881	1.820	1.876	1.822	1.864
283.15	2.266	2.218	2.228	2.219	2.200	2.034	1.994	2.022	1.996	2.000	1.861	1.809	1.864	1.811	1.853
293.15	2.238	2.201	2.212	2.203	2.183	2.023	1.978	2.005	1.980	1.983	1.847	1.793	1.847	1.795	1.836
298.15	2.234	2.195	2.206	2.196	2.177	2.013	1.972	1.998	1.974	1.976	1.842	1.788	1.840	1.789	1.829
303.15	2.236	2.190	2.200	2.191	2.172	2.007	1.967	1.992	1.968	1.970	1.834	1.782	1.835	1.784	1.823
313.15	2.230	2.182	2.192	2.183	2.164	2.005	1.960	1.984	1.961	1.963	1.826	1.776	1.826	1.778	1.815
323.15	2.224	2.181	2.190	2.182	2.162	2.006	1.959	1.983	1.960	1.960	1.823	1.777	1.824	1.779	1.814
	w_1 = 7.50 %					w_1 = 10.00 %					w_1 = 20.0 %				
278.15	1.764	1.697	1.782	1.699	1.781	1.610	1.600	1.714	1.602	1.724	1.301	1.305	1.540	1.307	1.596
283.15	1.740	1.686	1.770	1.689	1.769	1.595	1.589	1.702	1.592	1.712	1.286	1.296	1.528	1.299	1.584
293.15	1.714	1.672	1.753	1.674	1.752	1.570	1.576	1.685	1.578	1.695	1.263	1.287	1.511	1.290	1.567
298.15	1.709	1.666	1.746	1.668	1.746	1.563	1.571	1.678	1.573	1.688	1.262	1.285	1.504	1.288	1.560
303.15	1.703	1.662	1.740	1.664	1.740	1.557	1.567	1.672	1.569	1.682	1.251	1.284	1.498	1.287	1.554
313.15	1.693	1.657	1.732	1.659	1.732	1.551	1.563	1.664	1.565	1.674	1.250	1.285	1.490	1.288	1.546
323.15	1.693	1.658	1.730	1.661	1.730	1.555	1.566	1.662	1.568	1.672	1.251	1.294	1.488	1.297	1.544
malic acid (2) + water (2)															
T (K)	w_1 = 0.98 %					w_1 = 2.45 %					w_1 = 4.90 %				
278.15	2.340	2.310	2.322	2.311	2.293	2.100	2.089	2.118	2.090	2.095	1.950	1.903	1.962	1.905	1.949
283.15	2.325	2.298	2.310	2.299	2.281	2.083	2.076	2.106	2.078	2.083	1.920	1.891	1.950	1.893	1.936
293.15	2.317	2.287	2.299	2.288	2.270	2.062	2.066	2.095	2.067	2.072	1.902	1.882	1.939	1.883	1.926
298.15	2.310	2.281	2.292	2.282	2.264	2.058	2.060	2.088	2.061	2.065	1.897	1.876	1.932	1.877	1.919
303.15	2.311	2.279	2.290	2.279	2.261	2.053	2.058	2.085	2.059	2.062	1.893	1.874	1.929	1.875	1.916
313.15	2.313	2.275	2.286	2.276	2.257	2.052	2.055	2.082	2.056	2.059	1.891	1.872	1.926	1.874	1.912
323.15	2.315	2.277	2.287	2.278	2.258	2.049	2.057	2.083	2.058	2.060	1.893	1.875	1.926	1.877	1.913
	w_1 = 7.35 %					w_1 = 9.80 %					w_1 = 19.60 %				
278.15	1.830	1.780	1.869	1.782	1.866	1.699	1.682	1.802	1.684	1.809	1.380	1.382	1.630	1.384	1.680
283.15	1.810	1.768	1.856	1.770	1.853	1.687	1.670	1.789	1.672	1.796	1.360	1.372	1.617	1.374	1.667
293.15	1.784	1.759	1.846	1.761	1.842	1.675	1.662	1.778	1.664	1.785	1.355	1.369	1.606	1.371	1.656
298.15	1.781	1.754	1.839	1.756	1.836	1.666	1.657	1.771	1.659	1.778	1.350	1.367	1.599	1.369	1.649
303.15	1.782	1.752	1.836	1.754	1.833	1.665	1.657	1.768	1.658	1.775	1.348	1.368	1.597	1.371	1.646
313.15	1.775	1.752	1.832	1.754	1.829	1.662	1.657	1.765	1.659	1.772	1.360	1.375	1.593	1.377	1.642
323.15	1.781	1.756	1.833	1.758	1.830	1.664	1.663	1.766	1.665	1.772	1.380	1.386	1.594	1.388	1.643
malonic acid (1) + water (2)															
T (K)	w_1 = 1.00 %					w_1 = 2.50 %					w_1 = 5.00 %				
278.15	1.947	1.959	1.969	1.957	1.956	1.720	1.733	1.758	1.732	1.751	1.532	1.548	1.598	1.548	1.601
283.15	1.944	1.953	1.963	1.951	1.950	1.714	1.727	1.752	1.726	1.745	1.531	1.543	1.592	1.542	1.595
293.15	1.939	1.945	1.955	1.943	1.941	1.710	1.719	1.744	1.718	1.737	1.525	1.535	1.584	1.535	1.587
298.15	1.936	1.943	1.953	1.941	1.940	1.710	1.718	1.742	1.717	1.735	1.530	1.534	1.582	1.534	1.585
303.15	1.938	1.944	1.954	1.943	1.941	1.712	1.719	1.743	1.718	1.736	1.530	1.536	1.583	1.535	1.585
313.15	1.950	1.951	1.961	1.949	1.947	1.718	1.727	1.750	1.726	1.743	1.534	1.545	1.590	1.544	1.593
323.15	1.953	1.968	1.977	1.966	1.964	1.727	1.745	1.766	1.744	1.759	1.545	1.564	1.607	1.563	1.609
	w_1 = 7.50 %					w_1 = 10.00 %					w_1 = 20.0 %				
278.15	1.424	1.428	1.504	1.428	1.516	1.320	1.334	1.435	1.334	1.458	1.045	1.055	1.261	1.054	1.326
283.15	1.417	1.423	1.497	1.422	1.510	1.310	1.329	1.429	1.329	1.451	1.035	1.052	1.255	1.051	1.319
293.15	1.406	1.416	1.489	1.416	1.501	1.307	1.324	1.420	1.323	1.443	1.030	1.051	1.246	1.050	1.311
298.15	1.405	1.416	1.487	1.415	1.500	1.306	1.323	1.418	1.323	1.441	1.030	1.053	1.244	1.052	1.309
303.15	1.406	1.418	1.488	1.418	1.501	1.310	1.326	1.419	1.326	1.442	1.030	1.058	1.245	1.057	1.310
313.15	1.415	1.428	1.495	1.427	1.508	1.323	1.337	1.426	1.337	1.449	1.040	1.073	1.252	1.073	1.317
323.15	1.430	1.448	1.512	1.447	1.524	1.330	1.358	1.443	1.358	1.466	1.050	1.099	1.270	1.099	1.334

Table 3.5
pH data of polycarboxylic acid (1) + water (2) solutions: (exp.) experimental data, predicted data by (A) UNIFAC-Lyngby+ Debye-Hückel term modified by Pitzer [7], (B) modified Debye-Hückel term [7], (C) UNIFAC-Lyngby and (id.) ideal assumption (w_1 % by mass)

	exp.	(A)	(B)	(C)	id.	exp.	(A)	(B)	(C)	id.	exp.	(A)	(B)	(C)	id.
oxalic acid (1) + water (2)															
T (K)	w_1 = 1.00 %					w_1 = 2.50 %					w_1 = 5.00 %				
278.15	1.281	1.260	1.267	1.232	1.222	0.995	0.996	1.008	0.975	0.975	–	–	–	–	–
283.15	1.276	1.264	1.271	1.236	1.226	1.002	1.000	1.013	0.979	0.979	0.819	0.806	0.826	0.792	0.807
293.15	1.280	1.271	1.278	1.244	1.234	1.002	1.008	1.021	0.988	0.988	0.799	0.815	0.835	0.801	0.816
298.15	1.280	1.275	1.282	1.248	1.238	1.005	1.013	1.026	0.993	0.993	0.799	0.820	0.840	0.806	0.822
303.15	1.280	1.279	1.286	1.252	1.242	1.006	1.017	1.030	0.997	0.997	0.799	0.824	0.845	0.811	0.826
313.15	1.290	1.286	1.293	1.259	1.249	1.020	1.025	1.039	1.005	1.006	0.809	0.833	0.854	0.820	0.835
323.15	1.300	1.297	1.304	1.271	1.260	1.031	1.038	1.051	1.018	1.018	0.829	0.846	0.867	0.833	0.848
	w_1 = 7.50 %					w_1 = 10.00 %									
278.15	–	–	–	–	–	–	–	–	–	–					
283.15	–	–	–	–	–	–	–	–	–	–					
293.15	0.685	0.701	0.728	0.692	0.722	–	–	–	–	–					
298.15	0.680	0.706	0.733	0.697	0.727	0.592	0.623	0.657	0.618	0.662					
303.15	0.680	0.710	0.738	0.701	0.732	0.595	0.627	0.661	0.622	0.667					
313.15	0.690	0.719	0.747	0.710	0.741	0.602	0.636	0.671	0.631	0.676					
323.15	0.720	0.733	0.761	0.724	0.754	0.618	0.650	0.685	0.645	0.690					
succinic acid (1) + water (2)															
T (K)	w_1 = 0.95 %					w_1 = 1.90 %					w_1 = 2.85 %				
278.15	2.657	2.652	2.668	2.653	2.666	2.498	2.484	2.516	2.485	2.518	2.384	2.378	2.427	2.379	2.432
283.15	2.652	2.643	2.659	2.644	2.657	2.490	2.475	2.507	2.476	2.509	2.370	2.370	2.418	2.371	2.423
293.15	2.650	2.630	2.645	2.631	2.644	2.485	2.463	2.494	2.464	2.496	2.362	2.358	2.404	2.359	2.409
298.15	2.648	2.626	2.641	2.626	2.638	2.482	2.458	2.488	2.459	2.490	2.360	2.353	2.399	2.354	2.404
303.15	2.650	2.622	2.636	2.622	2.634	2.485	2.454	2.484	2.455	2.486	2.360	2.350	2.394	2.351	2.400
313.15	2.657	2.617	2.632	2.618	2.629	2.493	2.450	2.479	2.452	2.481	2.353	2.346	2.390	2.348	2.395
323.15	2.664	2.618	2.631	2.619	2.630	2.500	2.452	2.479	2.453	2.481	2.370	2.349	2.390	2.350	2.395
	w_1 = 3.80 %					w_1 = 4.75 %									
278.15	–	–	–	–	–	–	–	–	–	–					
283.15	2.300	2.290	2.353	2.291	2.362	–	–	–	–	–					
293.15	2.290	2.278	2.340	2.279	2.349	2.240	2.212	2.290	2.213	2.303					
298.15	2.286	2.274	2.335	2.275	2.344	2.230	2.209	2.285	2.209	2.297					
303.15	2.285	2.271	2.331	2.272	2.339	2.230	2.206	2.280	2.207	2.293					
313.15	2.290	2.269	2.326	2.270	2.334	2.232	2.204	2.276	2.206	2.288					
323.15	2.295	2.272	2.325	2.272	2.334	2.241	2.208	2.275	2.209	2.287					
tartaric acid (1) + water (2)															
T (K)	w_1 = 0.10 %					w_1 = 1.50 %					w_1 = 2.50 %				
278.15	2.601	2.667	2.683	2.670	2.619	2.034	2.022	2.034	2.025	2.009	1.935	1.900	1.920	1.902	1.899
283.15	2.585	2.658	2.674	2.661	2.611	2.015	2.012	2.025	2.015	1.999	1.908	1.890	1.910	1.893	1.889
293.15	2.567	2.645	2.660	2.648	2.598	2.013	1.997	2.009	2.000	1.984	1.891	1.875	1.895	1.878	1.874
298.15	2.561	2.641	2.657	2.644	2.595	2.008	1.993	2.006	1.996	1.980	1.878	1.871	1.891	1.874	1.870
303.15	2.560	2.637	2.653	2.640	2.591	2.002	1.989	2.001	1.991	1.975	1.878	1.866	1.886	1.869	1.865
313.15	2.560	2.634	2.649	2.637	2.589	2.009	1.986	1.998	1.988	1.972	1.875	1.863	1.883	1.866	1.862
323.15	2.563	2.636	2.652	2.639	2.591	2.014	1.988	2.000	1.990	1.974	1.877	1.866	1.885	1.868	1.864
	w_1 = 6.90 %					w_1 = 1.31 %					w_1 = 20.00 %				
278.15	1.632	1.633	1.689	1.637	1.687	1.406	1.428	1.537	1.432	1.561	1.245	1.258	1.430	1.262	1.485
283.15	1.619	1.623	1.679	1.627	1.677	1.373	1.418	1.527	1.422	1.551	1.202	1.249	1.420	1.253	1.475
293.15	1.596	1.608	1.664	1.612	1.661	1.358	1.404	1.512	1.408	1.535	1.204	1.235	1.404	1.240	1.459
298.15	1.592	1.605	1.660	1.608	1.657	1.354	1.401	1.508	1.405	1.531	1.194	1.233	1.400	1.237	1.455
303.15	1.586	1.600	1.655	1.604	1.652	1.360	1.396	1.502	1.401	1.526	1.190	1.229	1.395	1.234	1.450
313.15	1.588	1.598	1.652	1.602	1.649	1.368	1.396	1.499	1.400	1.523	1.197	1.230	1.392	1.235	1.447
323.15	1.589	1.601	1.653	1.605	1.651	1.367	1.400	1.501	1.404	1.525	1.201	1.237	1.393	1.241	1.448

First, it should be noted that 7.5 and 10 % oxalic acid mixtures (by mass) were not completely soluble at temperatures up to 283.15 and 293.15 K, respectively. Moreover, 3.80 and 4.80 % succinic acid mixtures (by mass) were not completely soluble at temperatures up to 278.15 and 283.15 K, respectively. These facts restricted the evaluation ranges of these polycarboxylic acids.

As expected, the pH data of aqueous polycarboxylic acid solutions decreased with an increasing of concentration. An increase of concentration of acids in solution raised the amount of free ion H^+, leading to a decrease of the pH. A comparison among the different aqueous polycarboxylic acids solutions revealed that the decrease of pH obeys the following order: succinic acid > malic acid > citric acid > tartaric acid > malonic acid > oxalic acid. This result is perfectly in agreement with the dissociation constant data obtained from literature (Table 3.3). If the pK value decreases, K increases, because $pK = -\log K$. Moreover, because K is a ratio of products and reagents, if K increases, there is an increasing of the products of the reaction, i.e, an increasing of ion H^+, that decreases the pH.

Also, there is an interdependence effect between the temperature and the kind of acid on the pH data. In the evaluated range, the pH of citric and malic acid solutions decreased with an increase of the temperature. However, the pH values of oxalic acid increased with an increase of temperature. Malonic, succinic and tartaric acid presented a minimum point in the behavior of the pH versus temperature, around 298.15 K for malic and succinic acids and around 313.15 K for tartaric acid. This result is also in agreement with the behavior of the dissociation constant (Table 3.3). In fact, electrolyte dissociation constant K and activity coefficient γ_i of species are temperature-dependent [13], affecting pH measures.

The mean-relative deviations of calculated pH data, by each approach, from experimental measurements are presented in Table 3.6, as well as the effect of solute concentration on deviations. The mean-relative deviations (σ) of the predicted data (D_{pred}) from experimental measures (D_{exp}) were calculated according to Eq. (3.30), where *n* is the number of observations of each concentration. Because Tables 3.4 and 3.5 presented no temperature-dependence on deviations, these values were not presented on Table 3.6.

$$\sigma\ (\%) = 100\ (\ \Sigma_n\ |\ D_{exp} - D_{pred}\ |\ /\ D_{exp}\ )\ /\ n \qquad (3.30)$$

Table 3.6
Mean-relative deviations σ (%) between predicted and experimental pH values given by: (A) UNIFAC-Lyngby + Debye-Hückel term modified by Pitzer [7], (B) modified Debye-Hückel term [7], (C) UNIFAC-Lyngby and (id.) ideal assumption. (w_1 % by mass)

citric acid (1) + water (2)				
w_1	(A)	(B)	(C)	id.
1.00	1.94	1.49	1.90	2.76
2.50	2.14	0.86	2.06	1.95
5.00	2.86	0.10	2.75	0.62
7.50	2.64	1.99	2.51	1.95
10.00	0.56	7.05	0.63	7.70
20.00	1.94	19.12	2.17	23.56
$\sigma(\%)$	2.01	5.10	2.00	6.42

malic acid (1) + water (2)				
w_1	(A)	(B)	(C)	id.
0.98	1.39	0.93	1.35	2.16
2.45	0.23	1.47	0.27	0.36
4.90	1.11	1.81	1.04	1.11
7.35	1.34	3.34	1.25	3.16
9.80	0.49	6.19	0.40	6.60
19.60	0.91	17.88	1.05	21.50
$\sigma(\%)$	0.91	5.27	0.89	5.82

malonic acid (1) + water (2)				
w_1	(A)	(B)	(C)	id.
1.00	0.41	0.90	0.32	0.26
2.50	0.65	2.02	0.57	1.62
5.00	0.74	3.81	0.69	3.99
7.50	0.75	5.74	0.71	6.64
10.00	1.37	8.53	1.34	10.24
20.00	2.49	20.86	2.43	27.07
$\sigma(\%)$	1.07	6.98	1.01	8.30

oxalic acid (1) + water (2)				
w_1	(A)	(B)	(C)	id.
1.00	0.62	0.41	2.73	3.51
2.50	0.56	1.79	1.50	1.49
5.00	2.39	4.41	1.28	2.57
7.50	3.30	7.29	2.02	6.39
10.00	5.31	11.00	4.46	11.94
$\sigma(\%)$	2.44	4.98	2.40	5.18

succinic acid (1) + water (2)				
w_1	(A)	(B)	(C)	id.
0.95	0.91	0.55	0.89	0.58
1.90	1.12	0.49	1.09	0.51
2.85	0.33	1.59	0.30	1.80
3.80	0.68	1.91	0.63	2.30
4.75	1.17	2.08	1.13	2.64
$\sigma(\%)$	0.85	1.32	0.81	1.57

tartaric acid (1) + water (2)				
w_1	(A)	(B)	(C)	id.
0.10	2.89	2.51	3.02	1.10
1.50	0.77	0.31	0.65	1.43
2.50	0.83	0.44	0.68	0.89
6.90	0.61	4.03	0.83	3.87
13.10	2.70	10.43	2.99	12.17
20.00	2.83	16.62	3.19	21.18
$\sigma(\%)$	1.77	5.72	1.89	6.77

Deviation from the ideal assumption ($\gamma_i = 1$) revealed the nonideality of the evaluated aqueous polycarboxylic acid solutions especially at high concentrations (higher than 5 % by mass). The mean-relative deviation of theoretical from experimental data showed that the UNIFAC-Lyngby model + Debye-Hückel term modified by Pitzer [7] provided significantly better accuracy in the predictions of pH of the systems up to 20 % by mass and from 278.15 to 323.15 K when compared to the utilization of modified Debye-Hückel term [7]. Relative deviations between experimental and calculated data for pH of aqueous solutions of polycarboxylic acids presented by Achard et al. [6] are, in general, higher than deviation data observed in this work. The following deviation data was presented by that author: 4.54 % for citric acid, 4.09 % for malic acid, 3.75 % for oxalic acid and 0.45 % for tartaric acid. Excepting for tartaric acid solution, deviations observed by the authors could be attributed to the following factors: i) the system of equations used in this work for the calculation of γ_i has a higher degree of freedom, i.e., a higher number of independent variables. This required the utilization of a computer-aided procedure that led to a higher accuracy. ii) The utilization of the Velezmoro and Meirelles [12] [COO^-] UNIFAC-Lyngby a_{ij} interaction parameter, that used aqueous polycarboxylic acids solutions data for the determination of the parameter. The global-relative deviation data presented by Maffia and Meirelles [9] (σ = 1.31 %) of predicted pH data from experimental measures for aqueous polycarboxylic acids solutions at 298.15 K is similar to those observed in this work (σ = 1.51%). Despite the similarity with the Maffia and Meirelles [9] approach, this work used another algorithm and evaluated the effect of temperature on pH data, i.e, used a higher number of variables that could lead to higher deviations, which did not occur.

The pH data of diluted systems (lower than 1 % acid by mass) were better predicted by modified Debye-Hückel term [7]. When ion concentration is low, the average distance between ions is large and only long-range Coulomb’s law attractions and repulsions between the ions are important. As ion concentration rises, ions begin to interact also with repulsive forces, leading to volume effects and with short-range attraction (van der Waals) forces [27]. Thus, it was supposed that, for higher concentration of polycarboxylic acid, there were only short-range interactions and the electrostatic forces had no contribution for γ_i* calculation. Probably, the modified Debye-Hückel term [7] had lower accuracy for prediction of long-range contribution of γ_i* at higher concentration (above 5 % acid by mass) of polycarboxylic acid. Moreover, the predicted pH by UNIFAC-Lyngby model was as accurate as the predicted data from combined model (UNIFAC-Lyngby + Debye-Hückel term modified by Pitzer [7]). This fact suggests, also, that solutions of weak electrolytes, such as polycarboxylic acids, have few long-range attractions and repulsions between the ions which is not predicted with precision by the evaluated models or the short-range forces are more important for γ_i* estimation.

3.3.3 Asymmetrical activity coefficients

Tables 3.5 and 3.6 show the asymmetrical activity coefficient of ion H^+ data of polycarboxylic acid + water whose calculation followed the approaches used for pH prediction: i) UNIFAC-Lyngby model + Debye-Hückel term modified by Pitzer [7], ii) modified Debye-Hückel term [7] and iii) UNIFAC-Lyngby model. The $\gamma_{H+}*$ data were presented at the same range of temperature and concentration of experimental measurements. Figures (3.4) and (3.5) show the temperature-dependence of the activity of the ionic species of each electrolyte for diluted and concentrated systems, calculated by UNIFAC-Lyngby + Debye-Hückel term proposed by Pitzer [7] (the most accurate model). Figure (3.6) compares the concentration-dependence of the $\gamma_{H+}*$ calculated by the different approaches and Figure (3.7) shows the temperature-dependence of the $\gamma_{H+}*$ and concentration of ion H^+ of a 5% acid solution (by mass), calculated by UNIFAC-Lyngby + modified Debye-Hückel term [7].

Table 3.7

Asymmetrical activity coefficient of ion H^+ of polycarboxylic acid (1) + water (2) solutions calculated by: (A) UNIFAC-Lyngby + Debye-Hückel term proposed by Pitzer [7], (B) modified Debye-Hückel term [7] and (C) UNIFAC-Lyngby at different temperatures T (K). w_1 (% by mass)

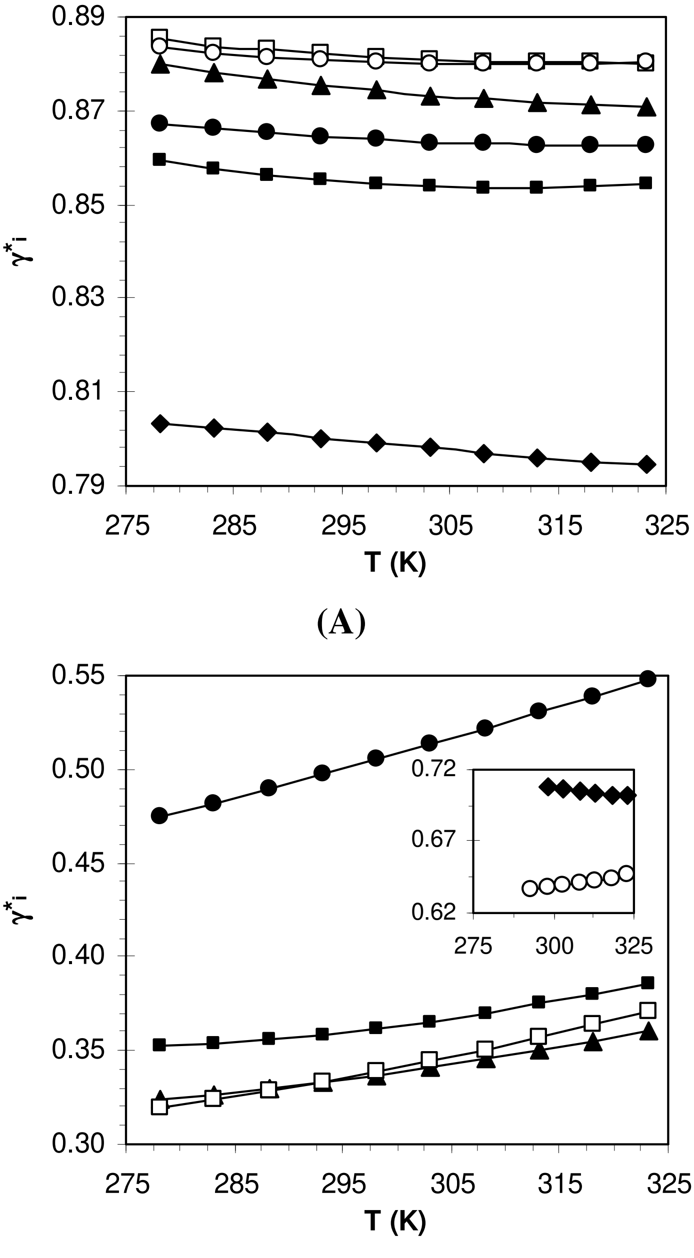
	Citric acid (1) + water (2)														
	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)
T(K)	w_1 = 1.00 %			w_1 = 5.00 %			w_1 = 10.00 %			w_1 = 15.00 %			w_1 = 20.00 %		
278.15	0.9258	0.9210	1.0058	0.9044	0.8871	1.0248	0.9008	0.8684	1.0504	0.9044	0.8558	1.0795	0.9129	0.8459	1.1132
283.15	0.9241	0.9192	1.0059	0.9023	0.8846	1.0253	0.8987	0.8656	1.0513	0.9025	0.8528	1.0809	0.9114	0.8426	1.1152
288.15	0.9227	0.9178	1.0060	0.9006	0.8826	1.0256	0.8969	0.8633	1.0520	0.9010	0.8503	1.0820	0.9102	0.8400	1.1169
293.15	0.9212	0.9162	1.0060	0.8987	0.8805	1.0259	0.8950	0.8608	1.0526	0.8992	0.8476	1.0831	0.9088	0.8371	1.1185
298.15	0.9200	0.9149	1.0061	0.8971	0.8785	1.0262	0.8933	0.8586	1.0531	0.8977	0.8452	1.0839	0.9076	0.8345	1.1198
303.15	0.9187	0.9135	1.0062	0.8954	0.8766	1.0264	0.8916	0.8565	1.0536	0.8962	0.8428	1.0847	0.9065	0.8321	1.1209
308.15	0.9176	0.9124	1.0062	0.8940	0.8751	1.0266	0.8903	0.8546	1.0540	0.8950	0.8409	1.0853	0.9056	0.8300	1.1219
313.15	0.9164	0.9112	1.0062	0.8924	0.8733	1.0267	0.8887	0.8526	1.0543	0.8936	0.8387	1.0859	0.9045	0.8277	1.1228
318.15	0.9156	0.9103	1.0063	0.8913	0.8720	1.0268	0.8876	0.8511	1.0545	0.8927	0.8370	1.0863	0.9039	0.8259	1.1234
323.15	0.9147	0.9093	1.0063	0.8902	0.8707	1.0269	0.8865	0.8496	1.0547	0.8917	0.8354	1.0867	0.9032	0.8241	1.1241
	Malic acid (1) + water (2)														
	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)
T(K)	w_1 = 0.98 %			w_1 = 4.90 %			w_1 = 9.80 %			w_1 = 15.00 %			w_1 = 19.60 %		
278.15	0.9286	0.9279	1.0014	0.8989	0.8967	1.0072	0.8825	0.8795	1.0151	0.8713	0.8678	1.0237	0.8624	0.8585	1.0332
283.15	0.9269	0.9262	1.0014	0.8965	0.8944	1.0072	0.8796	0.8768	1.0150	0.8682	0.8649	1.0235	0.8592	0.8554	1.0330
288.15	0.9257	0.9251	1.0014	0.8948	0.8928	1.0072	0.8777	0.8749	1.0149	0.8661	0.8628	1.0234	0.8570	0.8532	1.0327
293.15	0.9246	0.9240	1.0014	0.8932	0.8912	1.0071	0.8759	0.8731	1.0148	0.8642	0.8609	1.0232	0.8551	0.8512	1.0324
298.15	0.9234	0.9227	1.0014	0.8915	0.8894	1.0071	0.8739	0.8711	1.0147	0.8621	0.8586	1.0230	0.8529	0.8488	1.0322
303.15	0.9225	0.9218	1.0014	0.8901	0.8881	1.0071	0.8724	0.8695	1.0146	0.8605	0.8569	1.0228	0.8514	0.8470	1.0319
308.15	0.9216	0.9209	1.0014	0.8889	0.8868	1.0070	0.8710	0.8680	1.0145	0.8591	0.8553	1.0227	0.8500	0.8452	1.0316
313.15	0.9208	0.9200	1.0014	0.8877	0.8856	1.0070	0.8698	0.8666	1.0144	0.8578	0.8538	1.0225	0.8488	0.8436	1.0314
318.15	0.9201	0.9194	1.0014	0.8869	0.8847	1.0069	0.8688	0.8655	1.0143	0.8569	0.8526	1.0223	0.8480	0.8423	1.0311
323.15	0.9194	0.9186	1.0014	0.8859	0.8836	1.0069	0.8677	0.8642	1.0142	0.8559	0.8512	1.0222	0.8470	0.8408	1.0309
	Malonic acid (1) + water (2)														
	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)
T(K)	w_1 = 1.00 %			w_1 = 5.00 %			w_1 = 10.00 %			w_1 = 15.00 %			w_1 = 20.00 %		
278.15	0.9012	0.8980	1.0041	0.8603	0.8549	1.0117	0.8387	0.8320	1.0217	0.8265	0.8169	1.0348	0.8206	0.8051	1.0525
283.15	0.8998	0.8964	1.0043	0.8586	0.8527	1.0124	0.8374	0.8295	1.0230	0.8256	0.8141	1.0368	0.8201	0.8022	1.0551
288.15	0.8983	0.8948	1.0044	0.8571	0.8505	1.0130	0.8360	0.8270	1.0243	0.8246	0.8114	1.0386	0.8196	0.7993	1.0576
293.15	0.8972	0.8935	1.0045	0.8558	0.8487	1.0136	0.8350	0.8249	1.0253	0.8239	0.8092	1.0402	0.8194	0.7969	1.0597
298.15	0.8961	0.8923	1.0046	0.8546	0.8470	1.0140	0.8340	0.8230	1.0262	0.8233	0.8071	1.0415	0.8192	0.7947	1.0615
303.15	0.8953	0.8914	1.0047	0.8537	0.8457	1.0144	0.8334	0.8215	1.0270	0.8230	0.8055	1.0427	0.8192	0.7930	1.0630
308.15	0.8946	0.8907	1.0047	0.8530	0.8447	1.0147	0.8329	0.8203	1.0276	0.8229	0.8042	1.0436	0.8194	0.7916	1.0643
313.15	0.8941	0.8901	1.0048	0.8525	0.8439	1.0149	0.8326	0.8193	1.0281	0.8228	0.8030	1.0445	0.8197	0.7904	1.0655
318.15	0.8938	0.8899	1.0048	0.8522	0.8434	1.0151	0.8326	0.8187	1.0285	0.8231	0.8024	1.0452	0.8204	0.7897	1.0664
323.15	0.8938	0.8899	1.0048	0.8524	0.8434	1.0152	0.8331	0.8187	1.0288	0.8239	0.8023	1.0456	0.8214	0.7896	1.0670

Table 3.8
Asymmetrical activity coefficient of ion H^+ of polycarboxylic acid (1) + water (2) solutions calculated by: (A) UNIFAC-Lyngby + Debye-Hückel term proposed by Pitzer [7], (B) modified Debye-Hückel term [7] and (C) UNIFAC-Lyngby at different temperatures T (K). w_1 (% by mass)

	Oxalic acid (1) + water (2)														
	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)
T(K)	w_1 = 1.00 %			w_1 = 2.50 %			w_1 = 5.00 %			w_1 = 7.50 %			w_1 = 10.00 %		
278.15	0.8207	0.8035	1.0177	0.7891	0.7590	1.0297	–	–	–	–	–	–	–	–	–
283.15	0.8195	0.8022	1.0177	0.7879	0.7575	1.0300	0.7673	0.7223	1.0429	–	–	–	–	–	–
288.15	0.8183	0.8009	1.0178	0.7865	0.7560	1.0303	0.7661	0.7206	1.0436	–	–	–	–	–	–
293.15	0.8171	0.7998	1.0179	0.7853	0.7546	1.0305	0.7649	0.7190	1.0442	0.7554	0.6975	1.0548	–	–	–
298.15	0.8160	0.7986	1.0179	0.7840	0.7533	1.0307	0.7636	0.7175	1.0447	0.7543	0.6959	1.0557	0.7496	0.6803	1.0656
303.15	0.8148	0.7974	1.0179	0.7827	0.7519	1.0309	0.7624	0.7159	1.0453	0.7532	0.6942	1.0567	0.7486	0.6784	1.0670
308.15	0.8137	0.7963	1.0180	0.7814	0.7505	1.0310	0.7611	0.7143	1.0458	0.7520	0.6925	1.0576	0.7476	0.6766	1.0683
313.15	0.8125	0.7951	1.0180	0.7801	0.7491	1.0312	0.7597	0.7127	1.0463	0.7508	0.6908	1.0584	0.7465	0.6748	1.0696
318.15	0.8114	0.7940	1.0180	0.7788	0.7477	1.0313	0.7584	0.7112	1.0467	0.7495	0.6891	1.0592	0.7454	0.6731	1.0707
323.15	0.8106	0.7933	1.0179	0.7779	0.7470	1.0312	0.7574	0.7104	1.0466	0.7484	0.6883	1.0593	0.7443	0.6722	1.0710

	Succinic acid (1) + water (2)														
	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)
T(K)	w_1 = 0.95 %			w_1 = 1.90 %			w_1 = 2.85 %			w_1 = 3.80 %			w_1 = 4.75 %		
278.15	0.9524	0.9502	1.0031	0.9452	0.9416	1.0059	0.9409	0.9358	1.0087	–	–	–	–	–	–
283.15	0.9514	0.9492	1.0031	0.9441	0.9404	1.0059	0.9397	0.9346	1.0087	0.9365	0.9300	1.0116	–	–	–
288.15	0.9505	0.9484	1.0031	0.9431	0.9394	1.0059	0.9386	0.9335	1.0087	0.9353	0.9290	1.0116	–	–	–
293.15	0.9496	0.9474	1.0031	0.9421	0.9384	1.0059	0.9374	0.9324	1.0087	0.9341	0.9277	1.0116	0.9315	0.9239	1.0145
298.15	0.9489	0.9467	1.0031	0.9411	0.9374	1.0059	0.9364	0.9314	1.0087	0.9330	0.9266	1.0115	0.9304	0.9228	1.0144
303.15	0.9481	0.9459	1.0031	0.9403	0.9366	1.0059	0.9354	0.9303	1.0086	0.9320	0.9256	1.0115	0.9293	0.9217	1.0144
308.15	0.9474	0.9453	1.0031	0.9394	0.9358	1.0058	0.9345	0.9295	1.0086	0.9310	0.9247	1.0114	0.9282	0.9207	1.0143
313.15	0.9468	0.9446	1.0031	0.9386	0.9351	1.0058	0.9337	0.9287	1.0085	0.9301	0.9239	1.0113	0.9274	0.9198	1.0141
318.15	0.9463	0.9441	1.0030	0.9381	0.9345	1.0057	0.9330	0.9280	1.0084	0.9294	0.9231	1.0112	0.9266	0.9191	1.0140
323.15	0.9457	0.9436	1.0030	0.9375	0.9338	1.0057	0.9323	0.9274	1.0084	0.9287	0.9224	1.0111	0.9258	0.9183	1.0139

	Tartaric acid (1) + water (2)														
	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)
T(K)	w_1 = 0.10 %			w_1 = 1.50 %			w_1 = 6.90 %			w_1 = 13.10 %			w_1 = 18.40 %		
278.15	0.9449	0.9270	1.0473	0.9196	0.9023	1.0193	0.9388	0.8646	1.0876	0.9902	0.8446	1.1774	1.0674	0.8293	1.2970
283.15	0.9438	0.9258	1.0483	0.9178	0.9003	1.0194	0.9367	0.8619	1.0884	0.9883	0.8416	1.1792	1.0664	0.8261	1.3004
288.15	0.9428	0.9247	1.0494	0.9161	0.8985	1.0196	0.9346	0.8594	1.0891	0.9865	0.8388	1.1807	1.0654	0.8230	1.3036
293.15	0.9419	0.9236	1.0502	0.9145	0.8968	1.0197	0.9328	0.8572	1.0897	0.9849	0.8363	1.1821	1.0645	0.8203	1.3063
298.15	0.9411	0.9228	1.0509	0.9132	0.8954	1.0198	0.9312	0.8553	1.0902	0.9836	0.8342	1.1833	1.0639	0.8180	1.3087
303.15	0.9403	0.9219	1.0518	0.9118	0.8939	1.0199	0.9295	0.8532	1.0907	0.9820	0.8318	1.1844	1.0629	0.8154	1.3110
308.15	0.9397	0.9212	1.0526	0.9106	0.8926	1.0200	0.9280	0.8515	1.0911	0.9806	0.8298	1.1854	1.0621	0.8132	1.3129
313.15	0.9390	0.9205	1.0532	0.9096	0.8916	1.0201	0.9268	0.8500	1.0914	0.9796	0.8282	1.1862	1.0617	0.8114	1.3146
318.15	0.9386	0.9200	1.0536	0.9087	0.8907	1.0201	0.9258	0.8488	1.0916	0.9787	0.8268	1.1868	1.0614	0.8099	1.3161
323.15	0.9382	0.9195	1.0542	0.9078	0.8898	1.0201	0.9247	0.8475	1.0918	0.9778	0.8253	1.1874	1.0610	0.8083	1.3175



(A)

(B)

Fig. 3.4. Plot of γ_i* (by UNIFAC-Lyngby + Debye-Hückel term modified by Pitzer [7]) versus temperature T (K) of the ionic specie obtained from the first dissociation of each polycarboxylic acid solution: (■) malonic acid, (●) tartaric acid, (▲) citric acid, (□) malic acid, (○) succinic acid, (◆) oxalic acid. **(A)** solutions at 1 % and **(B)** 20 % polycarboxylic acid (by mass), except for oxalic acid (10 %) and succinic acid (4.75 %).

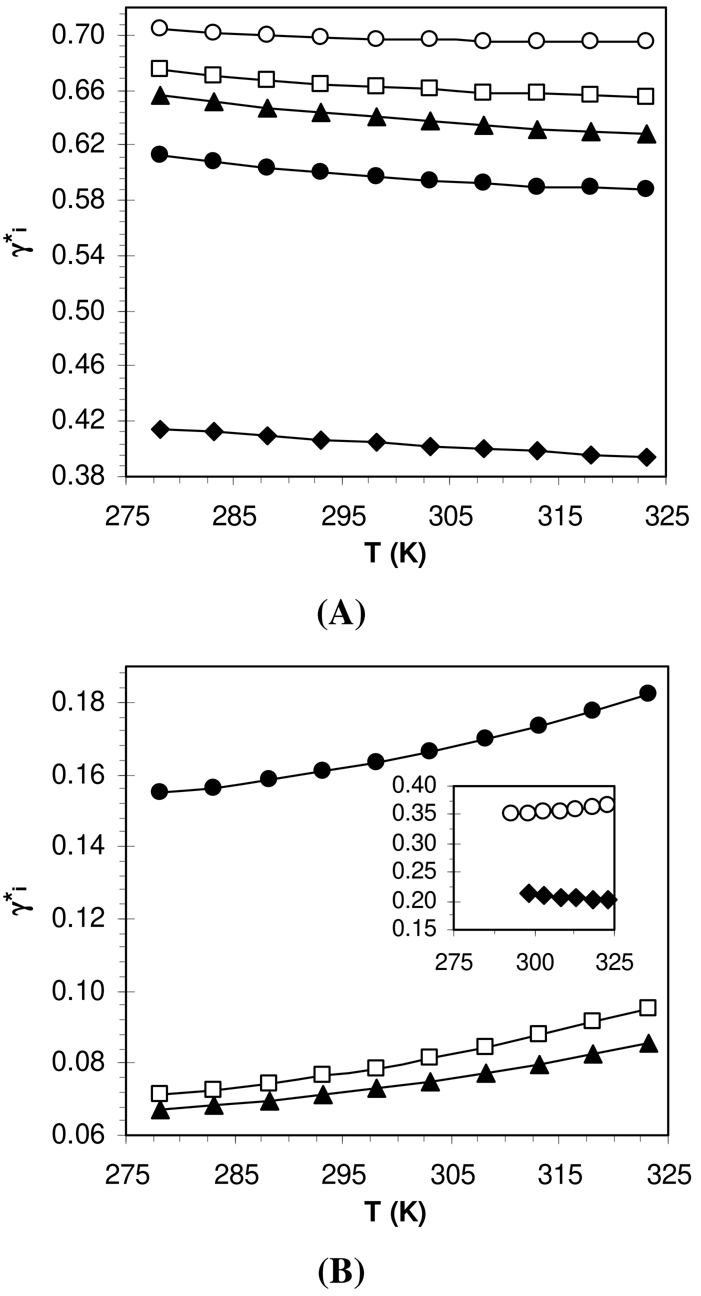
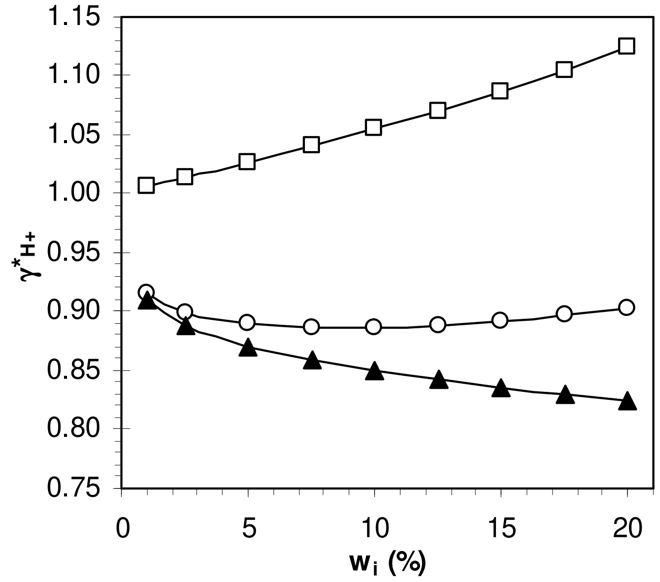
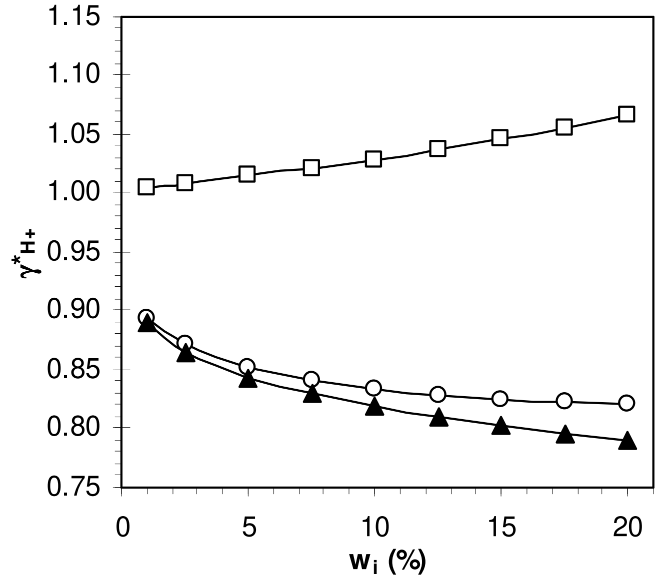


Fig. 3.5. Plot of γ_i* (by UNIFAC-Lyngby + Debye-Hückel term modified by Pitzer [7]) versus temperature T (K) of the ionic specie obtained from the second dissociation of each polycarboxylic acid solution: (■) malonic acid, (●) tartaric acid, (▲) citric acid, (□) malic acid, (○) succinic acid, (◆) oxalic acid. **(A)** solutions at 1 % and **(B)** 20% polycarboxylic acid (by mass), except for oxalic acid (10 %) and succinic acid (4.75 %).



(A)



(B)

Fig. 3.6. Plot of $\gamma_{H+}*$ versus w_i (% by mass) calculated by (□) UNIFAC-Lyngby, (○) UNIFAC-Lyngby + Debye-Hückel term modified by Pitzer [7] and (▲) modified Debye-Hückel term [7] for **(A)** citric acid solutions at 323.15 K and **(B)** malonic acid solutions at 323.15 K.

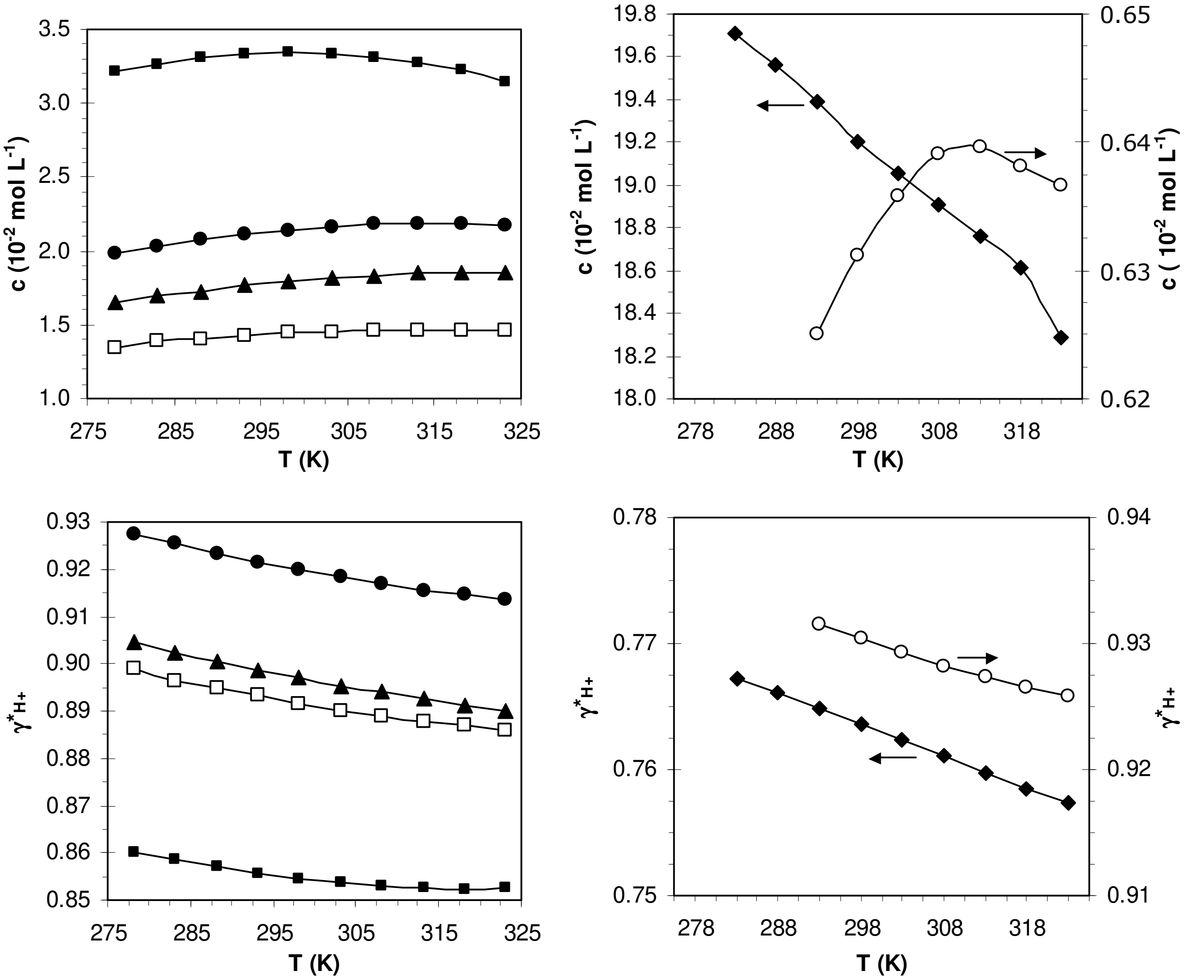


Fig. 3.7. Plot of concentration of ion H^+ c (10^{-2} mol L^{-1}) and $\gamma_{H+}*$ (by UNIFAC-Lyngby + Debye-Hückel term modified by Pitzer [7]) versus temperature T (K) of aqueous solutions with 5 % acid by mass: (■) malonic acid, (●) tartaric acid, (▲) citric acid, (□) malic acid, (○) succinic acid, (◆) oxalic acid.

It was observed that, in general, γ^*_{H+} calculated by UNIFAC-Lyngby model + Debye-Hückel term proposed by Pitzer [7] decreased with the increase of temperature (Tables 3.7 and 3.8). Also, once it was used the asymmetrical convention it was possible to assume that H^+ as well as the other chemical components of the solutions presented a negative deviation from the ideally dilute solution ($\gamma_i < 1$) for solutions up to 20 % (by mass). In general, for diluted solutions, the γ^* of ionic species decreased with temperature (Figs. 3.4A and 3.5A), i.e, the increasing of temperature raised the nonideality of the species. However, for concentrated solutions, this behavior changed (Figs. 4B and 5B). In fact, the comparison among the models for γ_i^* calculation (Fig. 3.6) showed that γ_{H+}^* calculated by UNIFAC-Lyngby model increased with concentration increasing and γ_{H+}^* calculated by modified Debye-Hückel term [7] decreased. This behavior is in agreement with the Coulomb's law where, in an aqueous electrolytic mixture, the electrostatic forces are inversely proportional to the distance, unlike physical and energetic interactions, i.e., while concentration increased, the long-range forces decreased and short-range forces increased.

The strong negative deviation of the ionic species (Figs. 3.4 and 3.5) showed that the free Gibbs energy (G) of the solutions is less than G from the corresponding ideal state, and the real solution could be more stable than it, and, probably, the interactions ion-ion are more favorable than the water-ion interactions. So, each ion tends to surround itself with ions of opposite charge, stabilizing the medium. However, at higher concentrations, the increasing of γ^* of ionic species (Figs. 3.4B and 3.5B) may be due to the hydration of ions that reduces the amount of free water molecules, thereby reducing the effective concentration of water and increasing the effective concentration of the electrolyte what reflected in the increase in γ^*, i.e, the solution becomes less stable [13].

Moreover, the increase of the ionic charge raised the nonideality, according to Fig. (3.4) and (3.5), where γ_i* of divalent ions are lower than the γ_i* of monovalent ions. In fact, the polycarboxylic acid ion, with its negative charge, forms stables internal hydrogen bounds and acts through the solvent medium with electrostatic forces [28] what probably led to the decrease of γ_i* and, consequently, the stabilization of the media (reducing of chemical potential of the solution).

According to the Le Chatelier's principle [13], the concentration of species in a chemical equilibrium is affected by temperature variation. Also, the γ_i* of the compounds in a mixture are temperature dependent [4]. Because pH depends on c_{H+} and $\gamma_{H+}*$, according to Eq. (3.14), data showed that, although temperature changes the chemical equilibrium and, consequently, the concentration of the species, the activity of the free hydrogen ion does not change at the same way. According to Fig. (3.7), the increasing of temperature led to a concentration increasing and a $\gamma*_{H+}$ decreasing, excepting for the behavior of the concentration of the free hydrogen ion of aqueous solutions of malonic, oxalic and succinic acids. Thermodynamically, the pH, that is the activity of a single ionic specie, is defined by Eq. (3.31) [26]

$$pH\,(X) = pH\,(S) - (\,E_X - E_S\,)\,F\,(2.303\,R\,T)^{-1} \tag{3.31}$$

where X is the sample, S is the electrode solution, E is the electromotive force (emf) of X or S, F and R are gas constants and T is temperature. It was expected that the increase of temperature would raise the electromotive force, the displacement of the chemical equilibrium, the dissociation of the electrolyte and the concentration of ion H^+ and, consequently, would reduced the pH. Also, as pH is proportional to T^{-1}, it was expected that the decrease of pH was more significant for lower temperatures. However, in general, this was not true, because the clear interdependence between concentration and activity of ion H^+.

3.3.4 Comparison with strong electrolyte solutions

The significance of short and long-range interactions, as well as the predictive ability of the UNIFAC-Lyngby model and Debye-Hückel term proposed by Pitzer [7] was also verified by the evaluation of the pH of aqueous hydrochloric acid solutions. Experimental pH data from 0.01 to 1.5 molal ($mol_{HCl}\ L_{water}^{-1}$) aqueous solutions of HCl (Synth, Brazil, 36.5 % by volume) was obtained at a temperature range from 278.15 to 323.15 K and from the same methodology applied for the polycarboxylic acids systems. This kind of solution was chosen because the almost complete dissociation of the electrolyte in aqueous solutions [29] and lower molecular weight than polycarboxylic acid, relevant for molecular interactions evaluation. The experimental data were compared with the predicted data obtained from: i) UNIFAC-Lyngby model + Debye-Hückel term modified by Pitzer [7], ii) modified Debye-Hückel term [7], iii) UNIFAC-Lyngby model, iv) activity coefficient data of ion H^+ related by Partanen and Covington [23] and v) ideal assumption. Table 3.9 shows the experimental and predicted results and Table 3.10 shows the mean-relative deviations (σ %) of the predicted from experimental data, calculated according Eq. (3.26).

Table 3.9

pH data of HCl + water solutions: (exp.) experimental data, predicted by (A) UNIFAC-Lyngby + Debye-Hückel term modified by Pitzer [7], (B) modified Debye-Hückel term [7], (C) UNIFAC-Lyngby, (D) activity coefficient data from Ref. [23] and (id.) ideal assumption. (m in $\text{mol}_{\text{HCl}}\ \text{L}_{\text{water}}^{-1}$)

	exp.	(A)	(B)	(C)	(D)	id.	exp.	(A)	(B)	(C)	(D)	id.
T (K)	m = 0.01						m = 0.10					
278.15	2.055	2.045	2.051	2.003	2.042	2.001	1.093	1.095	1.118	0.988	1.096	1.002
283.15	2.056	2.046	2.052	2.003	2.042	2.001	1.094	1.096	1.119	0.988	1.098	1.002
293.15	2.054	2.047	2.053	2.003	2.043	2.001	1.096	1.099	1.121	0.988	1.100	1.002
298.15	2.052	2.047	2.053	2.003	2.044	2.001	1.098	1.100	1.122	0.988	1.102	1.002
303.15	2.052	2.047	2.053	2.003	2.044	2.001	1.097	1.101	1.123	0.988	1.103	1.002
313.15	2.052	2.048	2.054	2.002	2.045	2.001	1.099	1.103	1.125	0.987	1.105	1.002
323.15	2.052	2.049	2.055	2.002	2.046	2.001	1.102	1.105	1.127	0.987	1.108	1.002
	m = 0.50						m = 1.00					
278.15	0.399	0.402	0.497	0.221	0.418	0.309	0.048	0.049	0.241	-0.168	0.090	0.016
283.15	0.394	0.403	0.499	0.221	0.421	0.309	0.050	0.051	0.243	-0.168	0.094	0.016
293.15	0.384	0.406	0.503	0.221	0.427	0.309	0.050	0.054	0.247	-0.169	0.102	0.016
298.15	0.386	0.408	0.505	0.220	0.430	0.309	0.055	0.056	0.249	-0.170	0.107	0.016
303.15	0.389	0.409	0.506	0.220	0.432	0.309	0.057	0.058	0.251	-0.170	0.111	0.016
313.15	0.401	0.413	0.510	0.220	0.438	0.309	0.059	0.061	0.256	-0.171	0.119	0.016
323.15	0.413	0.416	0.514	0.219	0.444	0.309	0.069	0.065	0.260	-0.172	0.128	0.016
	m = 1.50											
278.15	-0.195	-0.196	0.094	-0.436	-0.127	-0.153						
283.15	-0.185	-0.195	0.096	-0.436	-0.122	-0.153						
293.15	-0.171	-0.191	0.101	-0.438	-0.111	-0.153						
298.15	-0.172	-0.190	0.104	-0.438	-0.105	-0.153						
303.15	-0.165	-0.188	0.106	-0.439	-0.100	-0.153						
313.15	-0.154	-0.184	0.111	-0.440	-0.089	-0.153						
323.15	-0.164	-0.181	0.116	-0.441	-0.078	-0.153						

Table 3.10

Mean-relative deviation σ (%) of predicted from experimental pH data: (A) UNIFAC-Lyngby + Debye-Hückel term modified by Pitzer [7], (B) modified Debye-Hückel term [7], (C) UNIFAC-Lyngby, (D) activity coefficient data from Ref. [23] and (id.) ideal assumption. (m in $\text{mol}_{\text{HCl}}\ \text{L}_{\text{water}}^{-1}$)

m	(A)	(B)	(C)	(D)	id.
0.01	0.29	0.10	2.47	0.45	2.56
0.10	0.27	2.30	10.02	0.48	8.71
0.50	3.33	27.80	44.22	8.87	21.71
1.00	4.34	349.55	405.10	94.50	71.38
1.50	10.25	160.88	155.87	39.63	10.94
σ (%)	3.70	108.12	123.54	28.78	23.06

In general, the data showed that the pH increased with temperature increasing and this is more significant for concentrated solutions. The pH values of diluted systems were almost constant at the temperature range evaluated. The data is in agreement with the dissociation constants presented by Ref. [29] in which K decreased with the increase of the temperature (Table 3.11). The decreasing of K, decreases the amount of dissociated ionic species leading to pH rise. This behavior was also observed in oxalic acid systems, the most nonideal mixtures among the evaluated polycarboxylic acids solutions.

Table 3.11
Dissociation constant of hydrochloric acid [29]

T (K)	273.15	283.15	293.15	298.15	303.15	313.15	323.15
$K \cdot 10^{-6}$	20	6.8	2.4	1.3	0.72	0.28	0.13

Relative deviations data showed that, for high diluted systems (0.01 molal), modified Debye-Hückel term [7] had greater accuracy. Partanen and Covington [23] also used a kind of Pitzer equation (Eq. 3.32) for $\gamma_i{*}$ prediction, whose data is also accurate for diluted systems.

$$\ln \gamma_i{*} = (-3 A\phi m^{0.5})(1 + 1.4 m^{0.5})^{-1} + (0.30645 - 0.001006\, T)\, m \tag{3.32}$$

where A_ϕ is the Debye-Hückel parameter (the same of equation 3.12), T is the temperature (ºC) and m is the molal concentration of the electrolyte. The other constants were fitted by those authors. The UNIFAC-Lyngby model + Debye-Hückel term modified by Pitzer [7] had the greater global accuracy at the concentration range evaluated. However, the UNIFAC-Lyngby model was not able to accurately predict the pH of hydrochloric acid, whatever the concentration, unlike for aqueous polycarboxylic acid solutions. Because modified Debye-Hückel term [7] is a limiting law, this equation was useful for diluted systems of hydrochloric acid, unlike concentrated systems as it does not take into account short-range interactions, highly significant, in this case. Thus, the combined model is highly appropriate, accounting for both kinds of molecular interactions, short and long-range forces.

In fact, polycarboxylic acids solutions did not present significant long-range effects at concentrated systems. This suggests two theories: i) the molecular weight of the compound contributes to the existence or not of short or long-range forces, depending on concentration, ii) the dissociation ability and, consequently, the appearance of ionic species affects the chemical potential of the solution, making significant the short or long-range forces.

Table 3.12 presents the activity coefficient of ion H^+ calculated by the 4 aforementioned approaches and Fig. (3.8) represents the concentration-dependence of $\gamma_{H+}*$ data for HCl + water solutions at 323.15 K. The data showed similar behavior to that observed for aqueous polycarboxylic acids solutions. Debye-Hückel term proposed by Pitzer [7] and the combined model showed that hydrochloric acid solutions presented a negative deviation from ideality, i.e., the solution is more stable than the ideally dilute solution due to electrostatic stabilization. However, activity data from UNIFAC-Lyngby model presented a positive deviation, i.e., the stability of the solution decreases with the increase of concentration. In fact, as concentration increased, the short-range forces became more significant. If it was taken into account both kind of interactions, Table 3.12 and Fig. (3.8) showed that by the prediction of the combined model, activity coefficient decreased for diluted systems and increased for concentrated solutions, presenting a minimum point. This behavior is also in agreement with Coulomb's law, as previously observed for polycarboxylic acids mixtures and was also observed by several authors for strong electrolyte solutions [30, 31].

Moreover, as the activity coefficient of ion H^+ was near 1, the global-deviation of the ideal assumption was smaller than the other approaches, except deviation of the combined model. This was not significant to assume that this kind of solution was close to the ideal behavior. But, this observation suggests that the utilization of the modified Debye-Hückel term [7] or the UNIFAC-Lyngby model could lead to a high deviation from the experimental data, because, as observed, it should be considered the existence of both, short and long-range forces in this kind of solution, whatever the concentration. However, highly concentrated solutions presented high deviation, whatever the model, suggesting that strong electrolyte concentrated solutions could not be predicted by the considered approaches.

Table 3.12
Asymmetrical activity coefficient of ion H^+ data of HCl + water solutions, calculated by (A) UNIFAC-Lyngby + Debye-Hückel term modified by Pitzer [7], (B) modified Debye-Hückel term [7] and (C) UNIFAC-Lyngby. (D) activity coefficient data from Ref. [23] and m in $mol_{HCl}\ L_{water}^{-1}$.

	(A)	(B)	(C)	(D)	(A)	(B)	(C)	(D)	(A)	(B)	(C)	(D)
T (K)	m = 0.01				m = 0.10				m = 0.50			
278.15	0.9101	0.9067	1.0041	0.9081	0.8137	0.7812	1.0425	0.8038	0.8155	0.6608	1.2356	0.7771
283.15	0.9092	0.9058	1.0042	0.9071	0.8119	0.7794	1.0426	0.8015	0.8126	0.6581	1.2363	0.7721
288.15	0.9083	0.9049	1.0042	0.9062	0.8100	0.7775	1.0428	0.7991	0.8098	0.6554	1.2370	0.7671
293.15	0.9074	0.9041	1.0042	0.9053	0.8081	0.7756	1.0429	0.7967	0.8069	0.6527	1.2377	0.7622
298.15	0.9066	0.9032	1.0042	0.9043	0.8062	0.7737	1.0430	0.7944	0.8040	0.6501	1.2383	0.7572
303.15	0.9057	0.9023	1.0042	0.9034	0.8043	0.7718	1.0431	0.7920	0.8011	0.6474	1.2390	0.7523
308.15	0.9048	0.9014	1.0042	0.9024	0.8024	0.7699	1.0432	0.7897	0.7982	0.6447	1.2396	0.7474
313.15	0.9039	0.9005	1.0042	0.9015	0.8005	0.7680	1.0433	0.7873	0.7952	0.6421	1.2402	0.7425
318.15	0.9030	0.8997	1.0042	0.9006	0.7986	0.7661	1.0434	0.7849	0.7923	0.6394	1.2408	0.7376
323.15	0.9021	0.8988	1.0042	0.8996	0.7966	0.7641	1.0435	0.7826	0.7893	0.6367	1.2413	0.7328
	m = 1.00				m = 1.50							
278.15	0.9339	0.6073	1.5396	0.8428	1.1156	0.5771	1.9356	0.9423				
283.15	0.9303	0.6044	1.5413	0.8347	1.1114	0.5740	1.9387	0.9306				
288.15	0.9268	0.6014	1.5430	0.8267	1.1071	0.5709	1.9418	0.9190				
293.15	0.9232	0.5985	1.5446	0.8187	1.1028	0.5678	1.9447	0.9074				
298.15	0.9196	0.5955	1.5462	0.8108	1.0985	0.5647	1.9477	0.8961				
303.15	0.9159	0.5926	1.5478	0.8030	1.0941	0.5617	1.9505	0.8848				
308.15	0.9123	0.5896	1.5493	0.7952	1.0896	0.5586	1.9533	0.8738				
313.15	0.9086	0.5867	1.5507	0.7874	1.0851	0.5555	1.9560	0.8627				
318.15	0.9048	0.5837	1.5522	0.7798	1.0806	0.5525	1.9587	0.8519				
323.15	0.9010	0.5808	1.5536	0.7721	1.0759	0.5494	1.9613	0.8410				

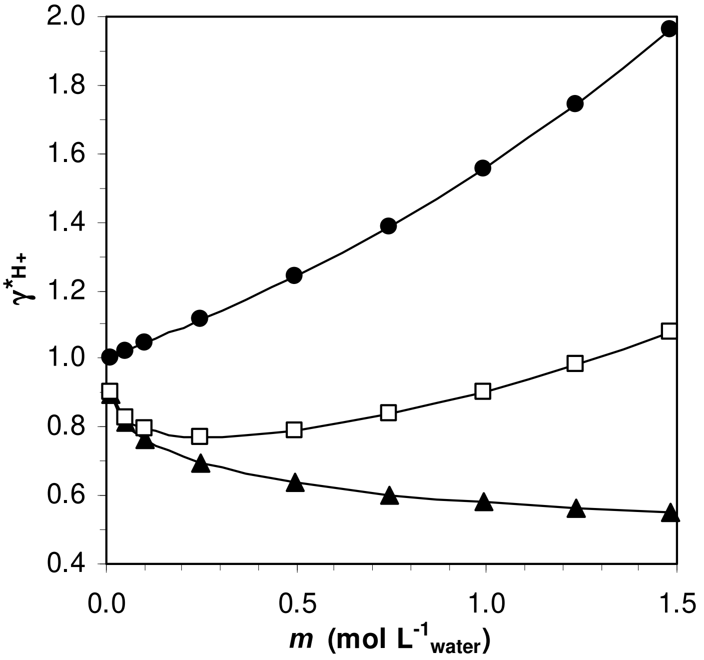


Fig. 3.8. Plot of γ^*_{H+} versus m (mol_{HCL} L^{-1}_{water}) at 323.15 K calculated by: (●) UNIFAC-Lyngby, (☐) UNIFAC-Lyngby + Debye-Hückel term modified by Pitzer (1980) and (▲) modified Debye-Hückel term [7].

3.4 Conclusions

The combined UNIFAC-Lyngby model + Debye-Hückel term modified by Pitzer [7] showed a good accuracy for the prediction of the activity coefficients and pH of aqueous polycarboxylic acids solutions up to 20 % by mass as well as aqueous hydrochloric acid solutions up to 1.50 molal at a temperature range from 278.15 to 323.15 K. Because of the long and short-range forces among the ions in solution, the use of activity coefficients in dealing with electrolyte solutions is essential, whatever the concentration, as modified Debye-Hückel term proposed by Pitzer [7] is well applied only for diluted systems and UNIFAC-Lyngby model does not take into account electrostatic interactions that affects the activity of the chemical species. In fact, pH of diluted hydrochloric and polycarboxylic acids were well predicted by modified Debye-Hückel term [7], while UNIFAC-Lyngby model was well applied for concentrated systems. However, pH prediction of concentrated hydrochloric acid solutions was well conducted by the summation of the long-range term in this model. Thus, the combined model UNIFAC-Lyngby model + Debye-Hückel term modified by Pitzer [7] is highly appropriated for prediction of activity-dependent thermodynamic properties of electrolyte solutions, accounting for both kind of molecular interactions, short and long-range forces.

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CONCLUSÕES

i) O rotaevaporador modificado com recirculação da fase vapor foi eficiente para a determinação da temperatura de ebulição de soluções aquosas de D-glucose e D-frutose e avaliação do efeito das baixas pressões e altas concentrações na variação desta propriedade. Os diagramas de Dühring, construídos a partir dos dados experimentais, foram suficientes para demonstrar a correlação positiva entre a pressão, concentração e temperatura de ebulição. Nas mesmas condições de pressão e concentração, a temperatura de ebulição de soluções de D-frutose é ligeiramente mais alta que as de soluções de D-glucose.

ii) O método de contribuição de grupos UNIFAC-Lyngby é útil para o cálculo do coeficiente de atividade de soluções aquosas de açúcares desde que seja levada em consideração a decomposição dos grupos químicos. Os grupos e parâmetros de interação propostos por Peres e Macedo (1997) obtiveram os melhores resultados na predição da temperatura de ebulição pois considera os agrupamentos cíclicos como grupos independentes.

iii) Foi possível observar que o efeito da temperatura no pH de soluções aquosas de ácidos policarboxílicos é dependente da concentração e da estrutura molecular dos ácidos. Para as mesmas condições de temperatura e concentração, a diminuição do pH é proporcional à seguinte ordem decrescente: ácido succínico, ácido malico, ácido cítrico, ácido tartárico, ácido malônico e ácido oxálico.

iv) O modelo combinado para cálculo do coeficiente de atividade de soluções de eletrólitos composto pelo modelo UNIFAC-Lyngby e pela equação moficada de Debye-Hückel é eficiente para a predição do pH das soluções aquosas de ácidos policarboxílicos. O modelo UNIFAC-Lyngby, que leva em consideração as interações moleculares de curto-alcance, foi suficiente para a predição das propriedades de soluções de ácidos orgânicos. O modelo combinado foi necessário quando as interações de longo-alcance foram relevantes, o que é o caso de ácidos fortes.

v) O algorítmo implementado em MATLAB foi preciso na predição da temperatura de ebulição de soluções aquosas de açúcares e pH de soluções de ácidos policarboxílicos. Implementado com a função de otimização fmincon, baseada no algorítmo para otimização de sistemas não-lineares SQP (Sequential Quadratic Programing) e no método numérico Quasi-Newton, em geral, produziu menores desvios relativos aos dados experimentais, quando estes foram comparados aos desvios apresentados pela literatura para sistemas semelhantes.

SUGESTÕES PARA TRABALHOS FUTUROS

i) Adequações construtivas no equipamento para medidas experimentais de temperatura de ebulição (rotaevaporador modificado com refluxo total da fase vapor): diminuição do volume do balão rotativo de ebulição da fase líquida e sua completa imersão no banho térmico de óleo de silicone de forma a assegurar uma menor variação da concentração durante o experimento devido à menor retenção de vapor condensado. Implementação de sistema de intrumentação e controle para monitoramento, aquisição e ajuste automatizado da pressão interna do equipamento.

ii) Realização de medidas experimentais e predição da temperatura de ebulição, através dos modelos para cálculo do coeficiente de atividade, de soluções aquosas binárias de pectina, soluções aquosas ternárias de ácidos policarboxílicos e açúcares e soluções modelo de sucos de fruta para contribuir com o banco de dados da literatura e na avaliação dos modelos preditivos.

iii) Realização de medidas experimentais e predição do pH de soluções aquosas de ácido trans-aconítico, ácido tricarboxílico presente em caldo de cana-de-açúcar, para contribuição com o banco de dados da literatura e processos da indústia sucro-alcooleira. Para isso, é necessária a determinação experimental das constantes de dissociação deste ácido como função da temperatura, dados inexistentes na literatura.