

Equação de Debye-Hückel

$$\log(\gamma_i) = -\frac{z_i^2 q^2 \kappa}{8\pi\epsilon_r \epsilon_0 k_B T} = -\frac{z_i^2 q^3}{4\pi(\epsilon_r \epsilon_0 k_B T)^{3/2}} \sqrt{\frac{I}{2}} = -A z_i^2 \sqrt{I}$$

z_i : número de cargas da espécie i

q : carga elementar

κ : comprimento de blindagem de Debye

ϵ_r : permissividade relativa do solvente

ϵ_0 : permissividade do espaço livre

k_B é a constante de Boltzmann

T é a temperatura da solução

I é a força iônica da solução

A é uma constante que depende do solvente.

Expressando I em termos da molalidade, $A = 1.172$
 $\text{mol}^{-1/2} \text{kg}^{1/2}$.

$$I = \frac{1}{2} \sum_{i=1}^n m_i z_i^2$$

Outro modo de representar não-idealidade: osmolaridade

$$\text{osmol/L} = \sum_i \varphi_i n_i C_i$$

- Mede-se a pressão osmótica de uma solução iônica de concentração molar C_i , formando n íons por molécula ou fórmula.

- Em uma solução ideal,

$$\pi = n_i C_i RT$$

- Em uma solução real, obtém-se a *osmolalidade*, da qual se obtém o coeficiente osmótico φ_i .

[IUPAC] Ionic Strength Corrections for Stability Constants - Windows Internet Explorer

http://www.iupac.org/web/ins/2000-003-1-500

File Edit View Favorites Tools Help


X pdfforge powered by YAHOO! SEARCH Search PDFCreator Options

X babylon Search and Translate Options

Favorites Free Hotmail Web Slice Gallery

http://www.iupac.org/web/ins/2000-003-1-500

Page Safety Tools



IUPAC

International Union of Pure and Applied Chemistry

Search

[Site Map](#) →

[Home](#)

[Projects](#)

[Publications](#)

[Conferences](#)

[Members and Bodies](#)

[Contacts](#)

[International Year of Chemistry](#)

[IUPAC Forums \(Members Only\)](#)

Projects by: [year](#) | [divisions and committees](#)

Project: Ionic Strength Corrections for Stability Constants

Objective

To facilitate the calculation of reliable stability constants for applications in an assortment of natural media (e.g. seawater, biological fluids).

To do this reliable activity coefficients must be available. This will be accomplished by preparing a computer based method for correcting stability constants for ionic strength changes in the range 0 - 5 mol dm⁻³ (with routines for converting to molal) using activity coefficients calculated from the Pitzer equation and Specific Interaction Theory (SIT). A database of published coefficients will be prepared and, where values are not available, they will be calculated using SIT approximations. The software will be made freely available on the web. It will not contain a critical evaluation of existing parameters.

Description

Currently the only general methods for calculating activity constants (and correcting stability constants) for changes in ionic strength are based on the Davies equation and Debye-Huckel theory. This equation is applicable only at low ionic strengths, particularly when ionic charges are above one. Hence it has very limited

Number: 2000-003-1-500

Start: 01 January 2000

End: 17 December 2005

Project of
[Analytical Chemistry Division](#)

Chair:
[Pettit, Leslie D.](#)

Members:
[Buzko, Vladimir](#)
[Puigdomenech, Ignasi](#)
[Sukhno, Igor](#)
[Wanner, Hans](#)

Internet 100%

start [IUP... Curs... Elect... Calc... BDT... Elect... Micr... PT Digite para pesqu... 16:05

[IUPAC] Ionic Strength Corrections for Stability Constants - Windows Internet Explorer

http://www.iupac.org/web/ins/2000-003-1-500

File Edit View Favorites Tools Help

X pdfforge powered by YAHOO! SEARCH Search PDFCreator Options

X babylon Search and Translate Options

★ Favorites ★ Free Hotmail Web Slice Gallery

[IUPAC] Ionic Strength Corrections for Stability Const...

version 1.2, released in Sep 2002, includes improved graph drawing routines and the list of SIT parameters have been extended to include those for many carboxylic acids. For a review of SIT, read about it in [Chem. Int. Nov 2002](#)

Version 1.5 was released in September 2003

- for Windows 9x, NT, 2000, and XP, download the following package > [SIT-v1.5-Sep03.zip](#) (zip file - 445KB)
- for a Russian version, download the following package > [SIT-v1.5-Sep03_Russian.zip](#) (zip file - 495KB)

For a review, read about it in [Chem. Int. Nov 2003](#)

> Nov 2004 report update ([pdf file - 12KB](#))

A suite of inter-linked programs - '**The Adjustment, Estimation and Uses of Equilibrium Constants in Aqueous Solution**' - has been developed and includes:

1. **SIT** program - Version 2.0 (2004)
2. **Electrolytes** - to calculate activity coefficients and water activity using Pitzer and Lin-Tseng-Lee equations.
3. **Acid-base** - to calculate acid-base equilibria in electrolytes and seawater for over 260 acids.
4. **Temperature Effects** - to calculate temperature dependence of log K values using 8 thermodynamic equations of increasing complexity.
5. **Oxygen solubility** - to calculate oxygen solubility in 22 electrolytes, natural fluids and seawater as a function of temperature, salinity etc.
6. **Speciation** - to calculate and display species distribution curves for complexes (including insolubles).
7. **Titration and speciation simulations** - to simulate titration curves in real time and display speciation dynamically.

For a review, read about it in [Chem. Int. May 2005](#)

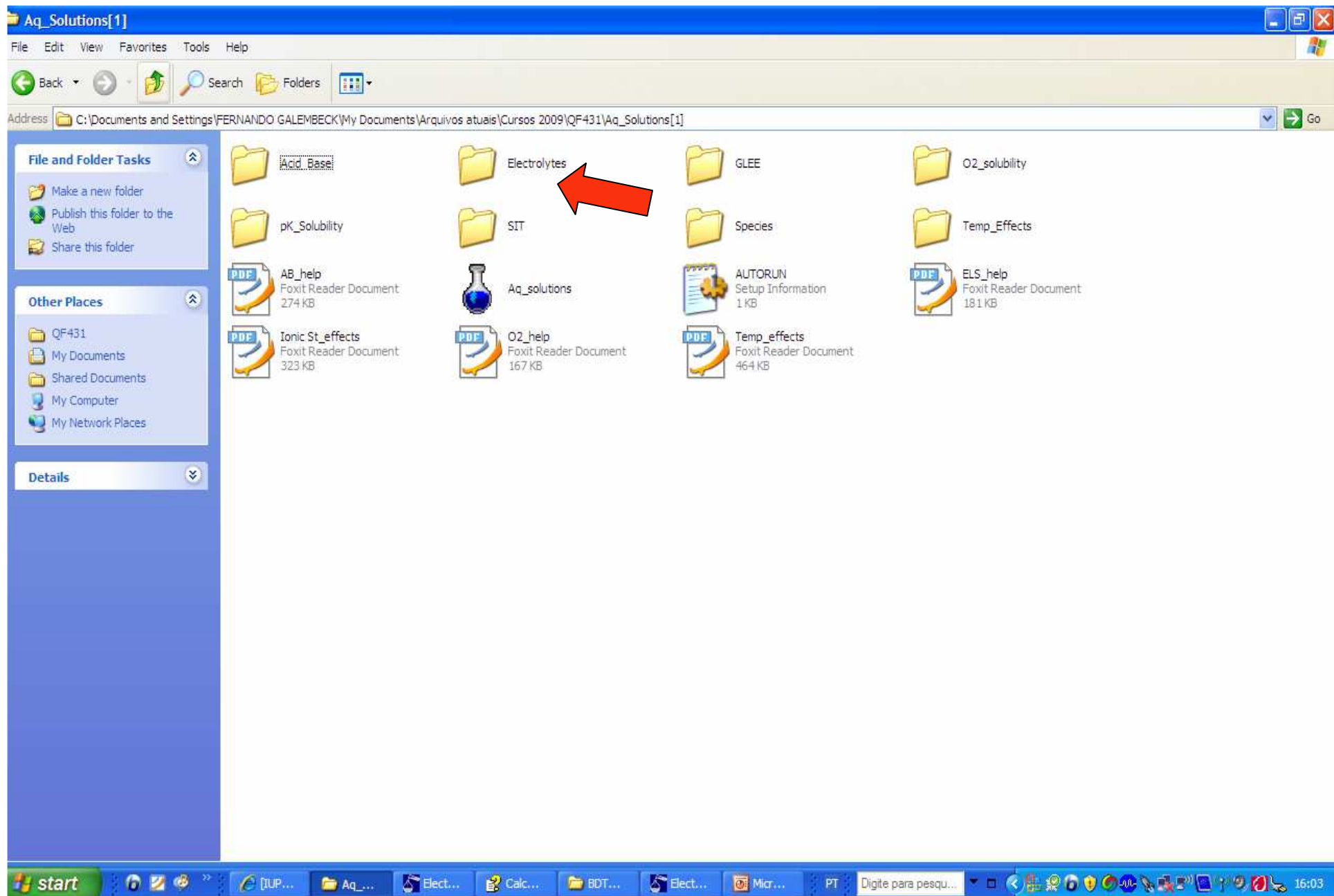
> download the entire suite > [Aq Solutions.zip](#) (zip file - 6.97MB)

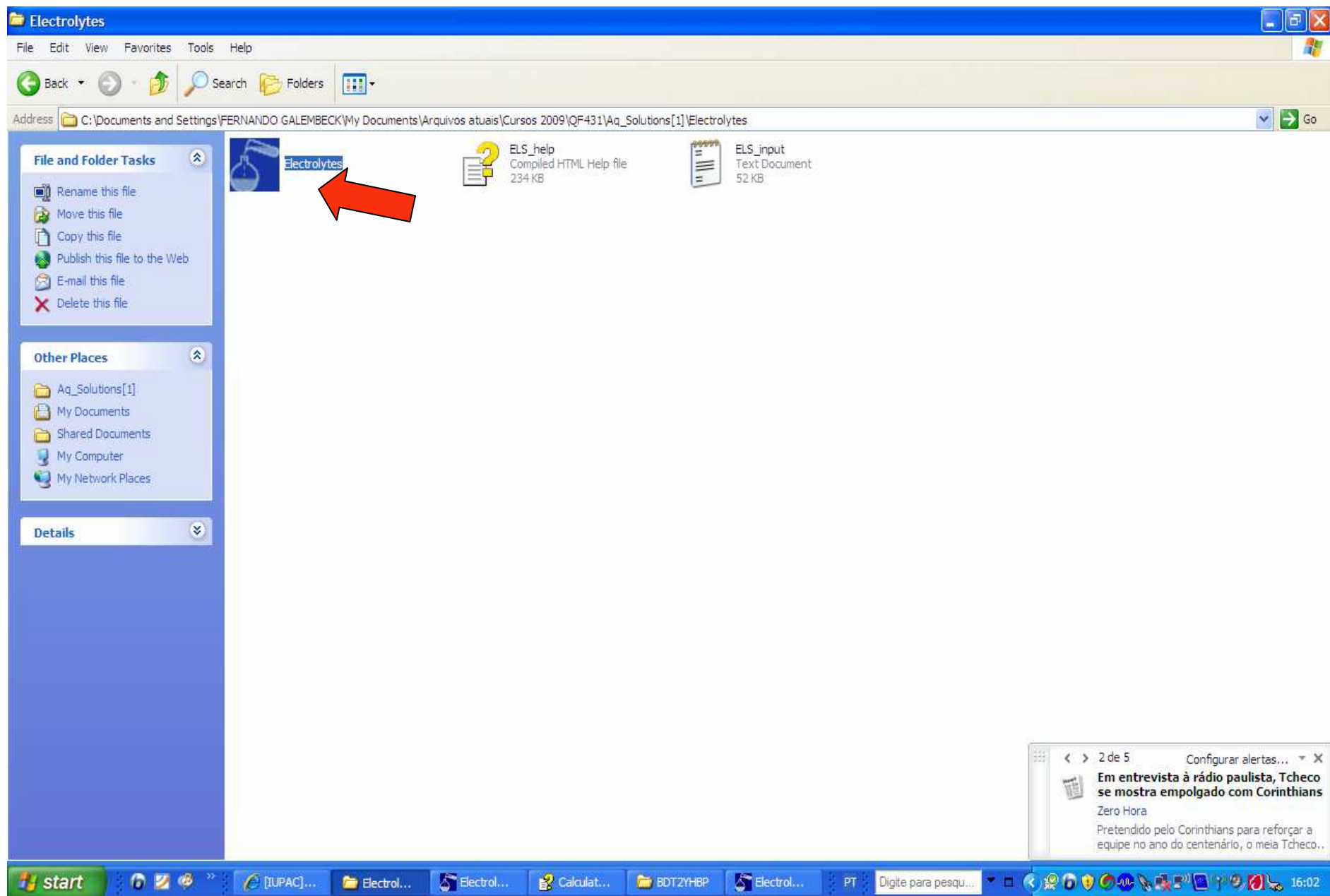
For more information, visit www.acadsoft.co.uk
questions/comments, e-mail L.D. Pettit <pettit@acadsoft.co.uk>

The current version of the suite of programs may also be downloaded from: public.kubsu.ru/aquasolsoft/ and select 'Projects'

Internet 100%

start [IUP... Curs... Elect... Calc... BDT... Elect... Micr... PT Digite para pesqu... 16:07





Calculation of

Thermodynamic properties of aqueous electrolyte solutions:

Electrolyte activity coefficients,
Osmotic coefficients and water activity,

using the

Pitzer-Mayorga and Lin-Tseng-Lee models

and the

Ionic activity coefficients in electrolyte solutions,

Ionic activity coefficients in seawater

using the

Millero-Pitzer method

Authors:

Vladimir Buzko

Igor Sukhno

Alexey Polushin



Aqua Solution Software

Russia, Krasnodar

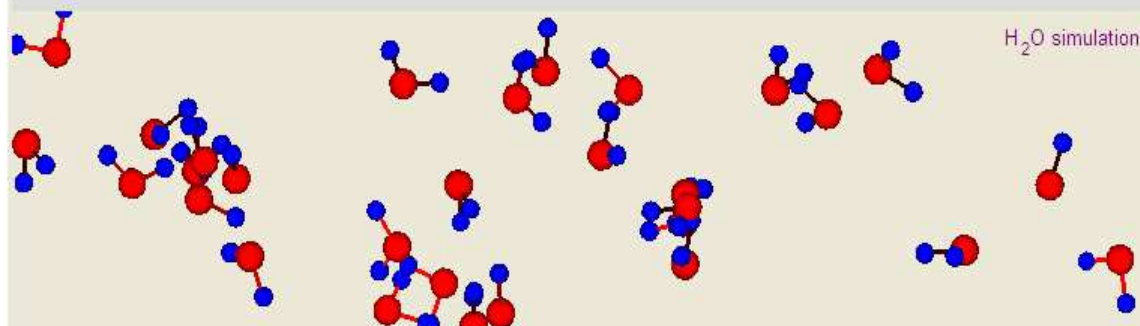
<http://public.kubsu.ru/AquaSolSoft>

e-mail: Sukhno@chem.kubsu.ru

e-mail: Buzko@chem.kubsu.ru

Expert Revision Leslie D. Pettit

Academic Software, UK www.acadsoft.co.uk



H₂O simulation

3. Select concentration range. 4. Select pump

KCl

$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	m_{\max}
0.04835	0.2122	-0.00084	4.80

b	\bar{D}_e	S	m_{\max}
4.849	61.553	0.032	4.50

0.00 — 0.90 Molal

50 ▼

Pitzer-Mayorga
Lin-Tseng-Lee

m	γ_{\pm}	$\lg \gamma_{\pm}$

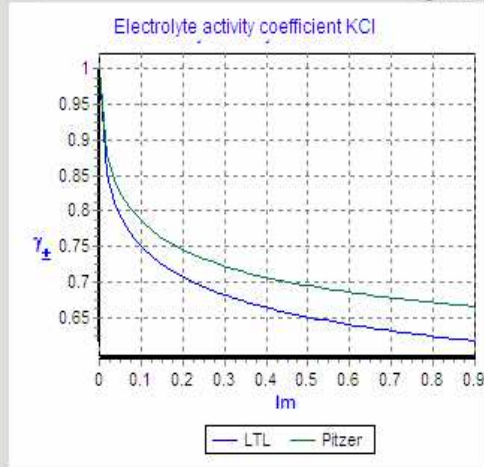
or

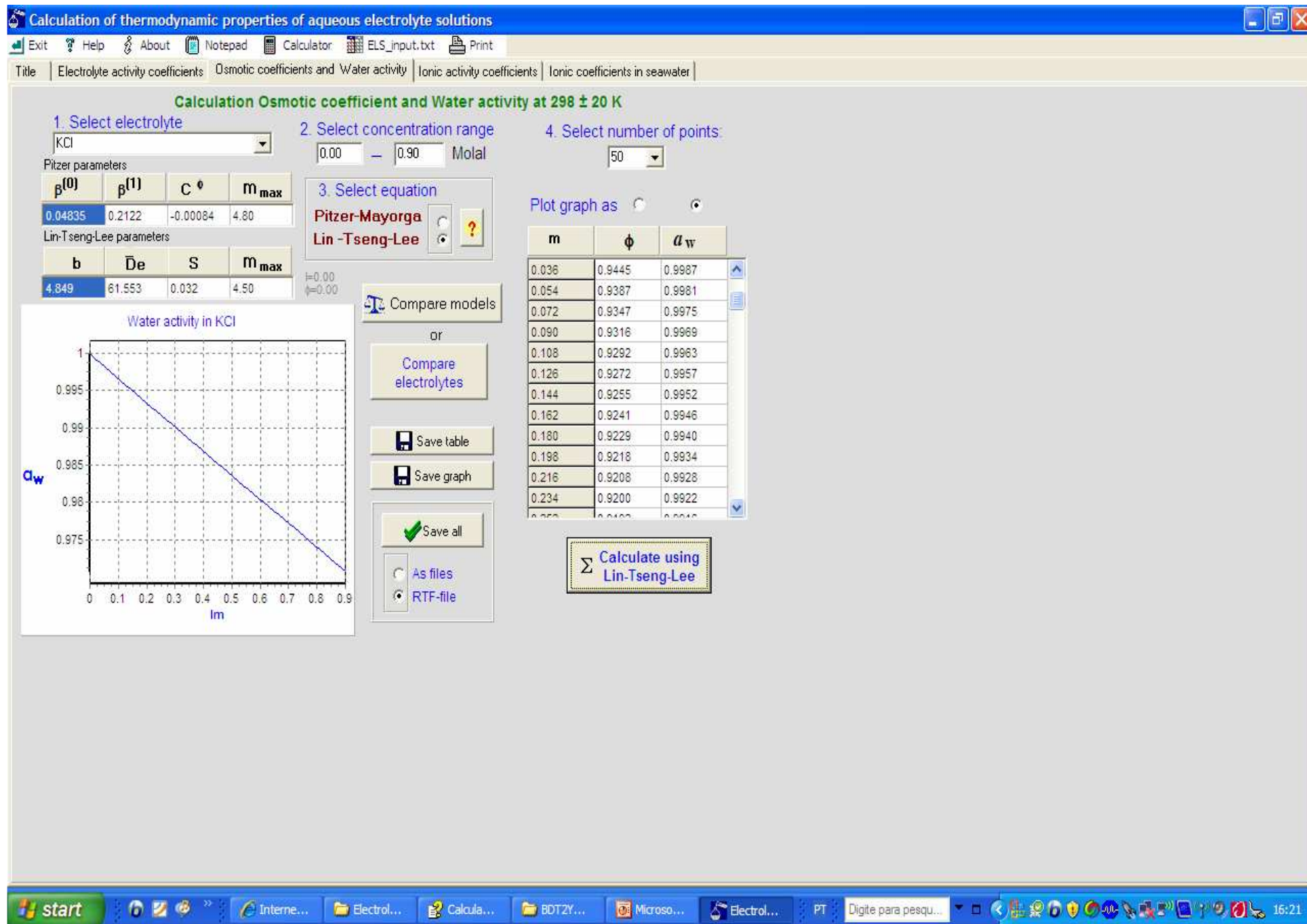
 Save table Save graph Save all

 As files

RTF-file

Σ Calculate using Pitzer-Mayorga





ELS_help - Foxit Reader 3.0 - [ELS_help]

File Edit View Language Document Tools Advanced Window Help

Modify your PDFs

Find:

The Pitzer-Mayorga equation [6] used to calculate the electrolyte activity coefficients is:

$$\ln \gamma_{\pm} = -|Z_m Z_x| A_{\phi} \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] + m \left(\frac{2\nu_M \nu_X}{\nu} \right) B_{MX}^{\gamma} + m^2 \frac{2(\nu_M \nu_X)^{3/2}}{\nu} C_{MX}^{\gamma},$$

where

$$B_{MX}^{\gamma} = 2\beta_{MX}^{(0)} + \frac{2\beta_{MX}^{(1)}}{\alpha^2 I} \left[1 - e^{-\alpha I^{1/2}} (1 + \alpha I^{1/2} - (1/2)\alpha^2 I) \right]$$

$$C_{MX}^{\gamma} = (3/2)C_{MX}^{\phi}$$

$$A_{\phi} = (1/3)(2\pi N_0 d_w / 1000)^{1/2} (e^2 / D_e kT)^{3/2}$$

Critically selected Pitzer parameters [25] were used in most cases.

The Lin-Tseng-Lee equation [22], which is also used to calculate the electrolyte activity coefficients, is:

$$\ln \gamma_{\pm} = \ln \gamma_{\pm}^{\text{pdh}} + \ln \gamma_{\pm}^{\text{sv}}$$

where

the Debye-Huckel term $\ln \gamma_{\pm}^{\text{(pdh)}}$ represents the Pitzer term:

$$\ln \gamma_{\pm}^{\text{pdh}} = -zwA_{\phi} \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right]$$

SV

Ready 6 / 14 152.46% Size: [8.26 * 11.69 in]

start Microsoft Power... [IUPAC] Ionic Str... Aq_Solutions[1] ELS_help - Foxit ... PT Digite para pesqu... 16:29

Questões

Estas questões devem ser respondidas usando o programa de cálculo de parâmetros de não-idealidade do projeto IUPAC. Cada resposta deve ser acompanhada de gráficos e dados numéricos que comprovem as afirmações da resposta. As respostas devem ser enviada pelo e-mail, sob o assunto “cálculos de atividade”

1. Compare dois eletrólitos 1:1, verificando até qual concentração eles obedecem à equação de Debye-Hückel.
2. Compare eletrólitos formados por íons com diferentes cargas (1:1, 1:2, 1:3...). Quando aumentam os desvios de não-idealidade?
3. Os coeficientes de atividade sempre diminuem, com o aumento da concentração do sal?
4. Examine alguns dados de atividade da água em soluções iônicas e extraia pelo menos uma conclusão.