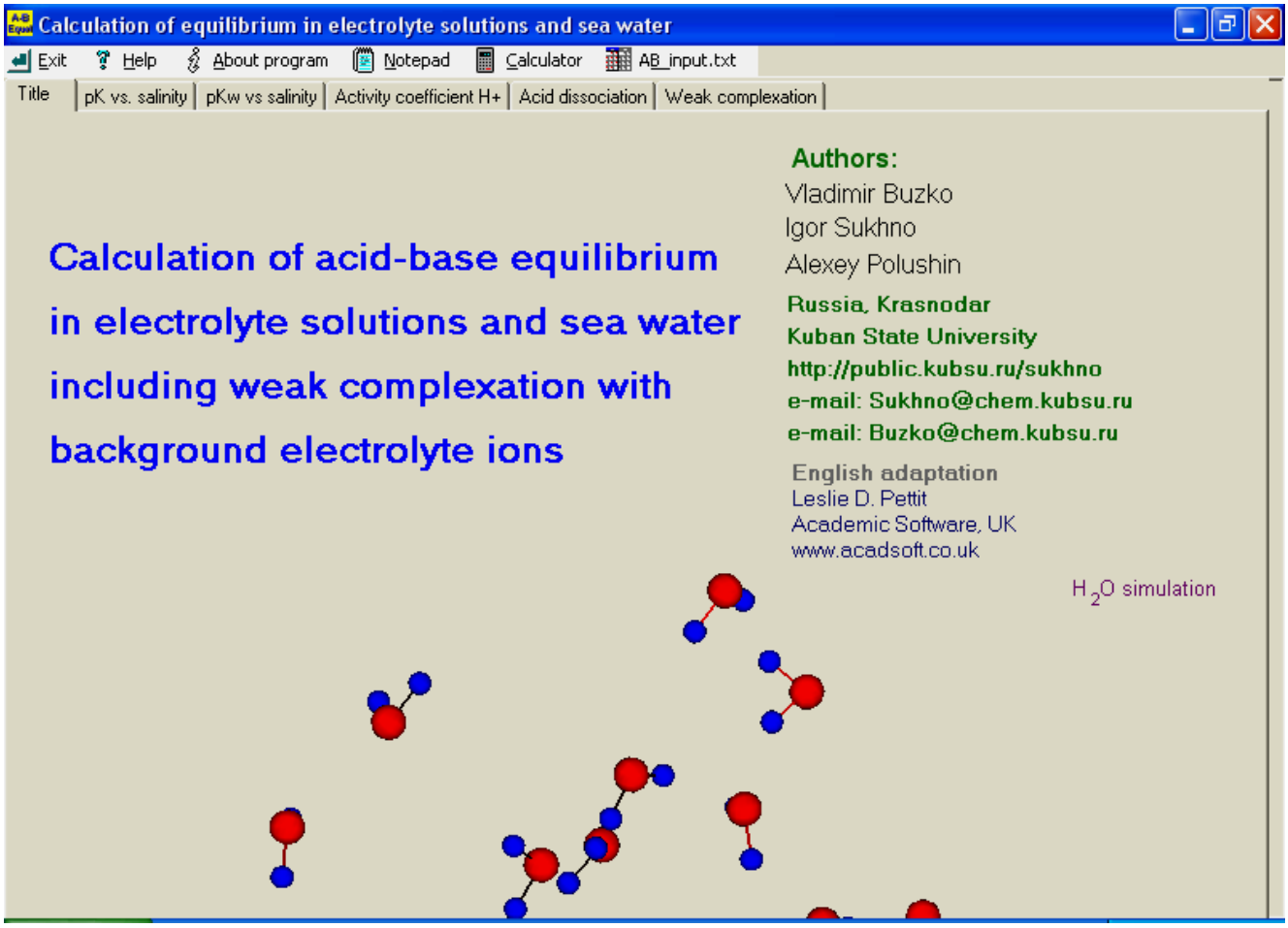
Manual


Calculation of equilibrium in electrolyte solutions and sea water
Exit
Help
About program
Notepad
Calculator
AB_input.txt
Title
pK vs. salinity
pKw vs salinity
Activity coefficient H+
Acid dissociation
Weak complexation
Calculation of acid-base equilibrium in electrolyte solutions and sea water including weak complexation with background electrolyte ions
Authors:
Vladimir Buzko
Igor Sukhno
Alexey Polushin
Russia, Krasnodar
Kuban State University
http://public.kubsu.ru/sukhno
e-mail: Sukhno@chem.kubsu.ru
e-mail: Buzko@chem.kubsu.ru
English adaptation
Leslie D. Pettit
Academic Software, UK
www.acadsoft.co.uk
H2O simulation

Introduction

Acid_Base is a program to calculate the acid-base equilibria in electrolyte solutions and sea water including the concept of weak complexation of plotolyte ionic forms with background ions. Program also allows to calculate the H^+ activity coefficient in different ionic media for correction equilibria pH values.
Calculation of acid-base dissociation equilibrium constants at different salinity is carried out by polynomial type equation. pKw values in sea water are calculated using the concept of weak complexation of OH^- ion with major cations of sea water. The H^+ activity coefficient in different ionic media is calculated using the Pitzer type equation. Acid dissociation constants in electrolyte solutions are calculated by the simplified Pitzer equation.

Acid_Base has been developed under the Windows 9x, 2000 and Windows NT/XP operating systems. The 32-bit version was built by Borland Delphi 5.0. The first version program was released on December 10, 2003 as version 1.0.

Acid_Base is composed of the following files:

- **Acid_base.exe** – the program exe-file
- **AB_input.txt** – input file
- **AB_help.chm** – the help file

If you have any suggestions, or know of any models and additional parameters that you would like to see added to the repertoire, please send us an e-mail. We will gladly attend to your comments since we wish to continue development and support of this program.

Russia, 350040 Krasnodar, Stavropolskaya Street 149,
Kuban State University, Department of General and Inorganic Chemistry
phone: +78612699574
fax: +78612699570
mobile*: +79184814558
e-mails: Sukhno@chem.kubsu.ru, Buzko@chem.kubsu.ru
Internet: http://public.kubsu.ru/sukhno

The authors express their sincere gratitude to
Dr. Leslie D. Pettit (Academic Software, UK, http://www.acadsoft.co.uk)
for his advice on designing this program.

Using the Acid_base.exe program

The **Acid_Base.exe** program has easy point-and-click interface and allows the user to

- Calculate the equilibrium dissociation constants of organic acids and bases at different salinity
- Calculate the pKw values at different salinity and at different temperature
- Calculate the H^+ activity coefficient (both molal and molar) in different ionic media
- Calculate the dissociation constants of organic acids at different concentration of background electrolytes and at different temperature
- Calculate the equilibrium molar fraction of ionic forms of polycarboxylic (mono-, di-, tri-, tetra-) acids at different pH
- Calculate the equilibrium molar fraction of free ionic forms of polycarboxylic (mono-, di-, tri-, tetra-) acids and the equilibrium molar fraction of weak complexes of ionic forms of polycarboxylic acids with ion background electrolyte at different pH
- Copy plots directly to the clipboard to use in another Windows application
- Save all results of calculation in Rich Text Format file
- Read simple ASCII data file
- Use a lot of thermodynamic dissociation constants (above 260 for acids and 10 for major amines and phenols)
- Use comments in input file and in the final RTF output
- Scale, translate, sort, remove and edit data sets by hand similarly to a spreadsheet
- Receive and to keep calculated information in a tabular and graphic form.

The **Acid_Base.exe** program has 5 main tabbed pages:

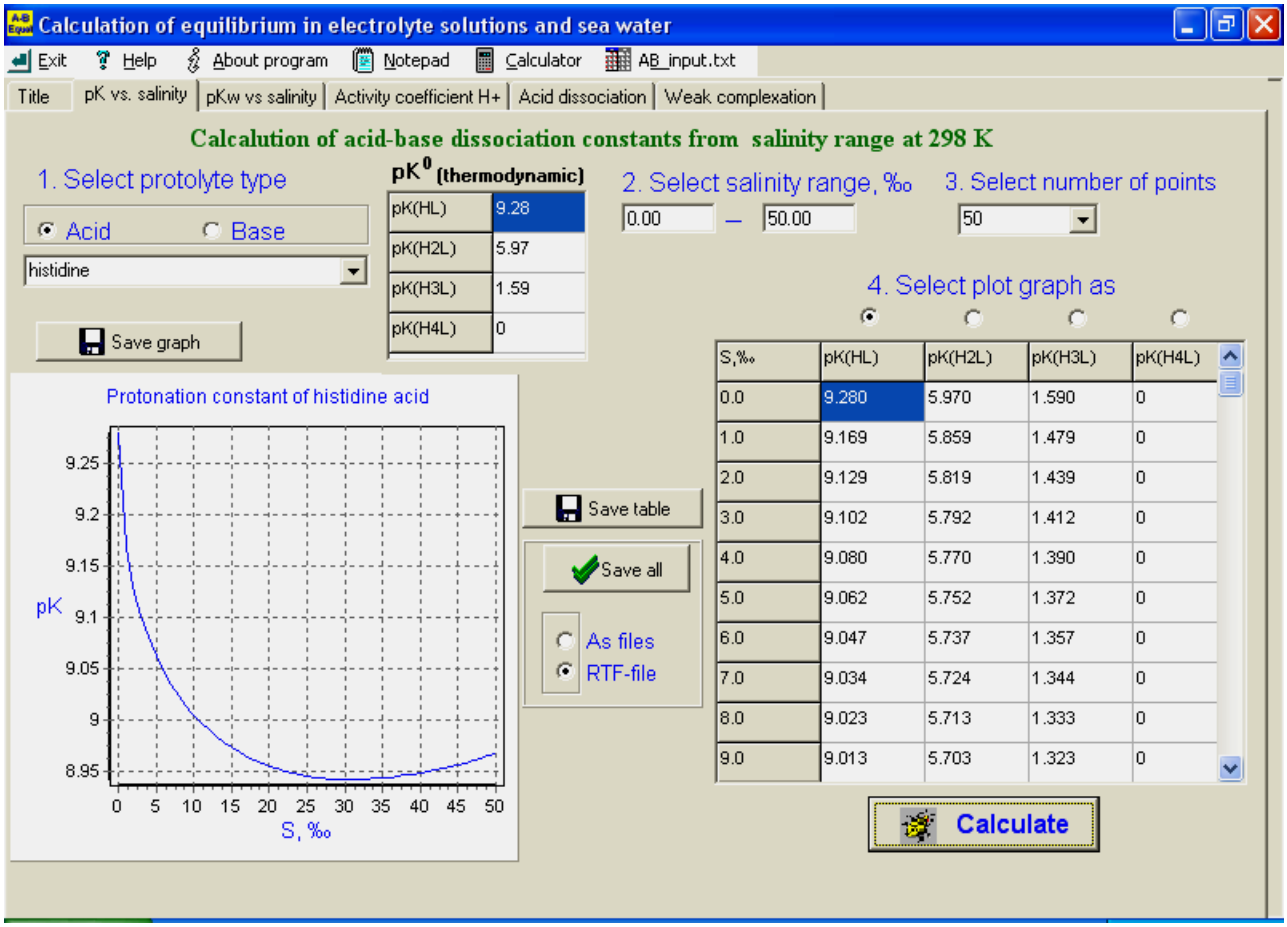
- **pK vs. salinity**
- **pKw vs. salinity**
- **Activity coefficient H^+**
- **Acid dissociation**
- **Weak complexation**

Like all Windows applications, you can also select items off of the menu bar to accomplish certain tasks.
The toolbar gives access to frequently used commands

- ✓ **Exit**
- ✓ **Help**
- ✓ **About**
- ✓ **Notepad**
- ✓ **Calculator**

pK vs. salinity

A ‘pK vs. salinity’ tabbed page is shown below



The dissociation constants of acids and bases in sea water are calculated by equation:

$$\lg K_j^* = \lg K_j^T + a_1 S^{1/2} + a_2 S + a_3 S^{3/2}$$

Data are taken from:
[1] - for polycarboxylic acids,
[2] - for phenols,
[3] - for aminoacids,
[4] - for polyamines.
Above equation is adequate in salinity range 0 - 50 ‰ (at 298 K) [5].
Parameters of equation are in **AB_input.txt** file.

Calculate and save results
To calculate dissociation constants of acids and bases in sea water

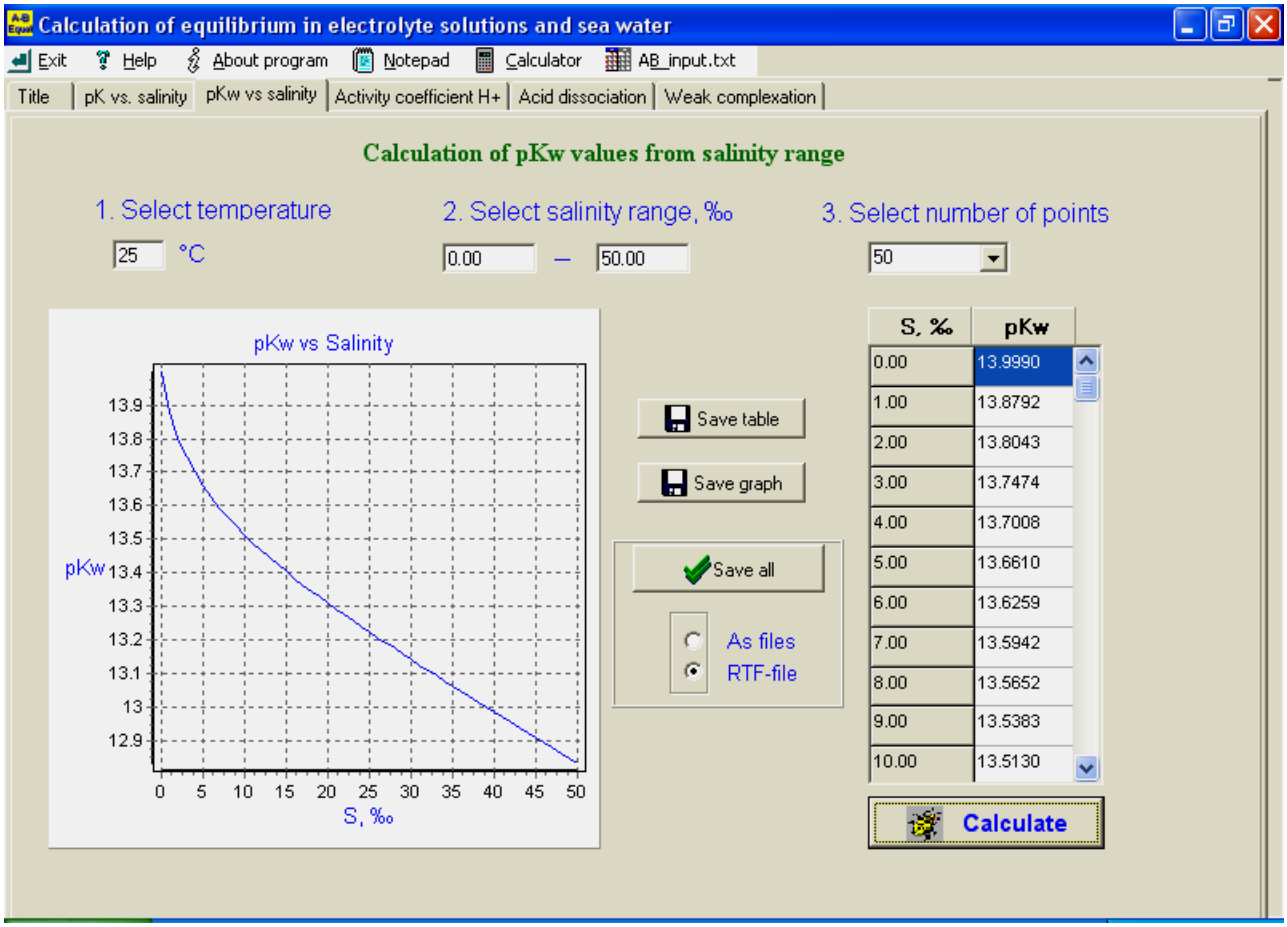
- Select acid or base from list
- Select salinity range
- Select the number of points
- Select desired type of "**Plot graph as**"
- Press the "**Calculate**" button

The user can save

- the table of the calculated values as a text file (***.txt**) and to the clipboard simultaneously
- the plot as a graphic file (***.bmp**) and to the clipboard simultaneously
- all results together (table, plot, comments) in RTF format

pKw vs. salinity

A ‘pKw vs. salinity’ tabbed page is shown below



The pKw values are calculated as a function of salinity. It is used **SSWE** (Synthetic Sea Water for Equilibrium studies) standard of artificial sea water to calculate the equilibrium ion concentrations of major sea water ions at different salinity values. For water the apparent dissociation constant pK* (HA) values are calculated by weak complexation concept (Sammartano S et al.) [6-7]:

$$pK_w^* = pK_w^O - \lg(1 + K^{NaOH}[Na^+] + K^{KOH}[K^+] + K^{MgOH}[Mg^{2+}] + K^{CaOH}[Ca^{2+}])$$

The thermodynamic pKw^0 values are calculated by equation [8]

$$pK_w^o = 13.999 - 3.295 \cdot 10^{-2} \cdot (t-25) + 1.8 \cdot 10^{-4} \cdot (t-25)^2 - 7.7 \cdot 10^{-7}(t-25)^3,$$

where complex formation constants K^{NaOH}, K^{KOH}, K^{MgOH}, K^{CaOH} are calculated by [9]

$$\lg K = \lg K_{25}^T + a_1(t-25) + a_2 S^{1/2} + a_3 S.$$

The equilibrium ion concentrations are calculated from total salinity **S.** The interactions between the major cations and anions of sea water are neglected. Uncertainty of calculated pKw values is close to 0.08 unit pKw in comparison with data [10-11].

Calculate and save results

To calculate the pKw values

- Indicate the temperature (from 0 to 50 °C)
- Select salinity range (from 0 to 50 ‰)

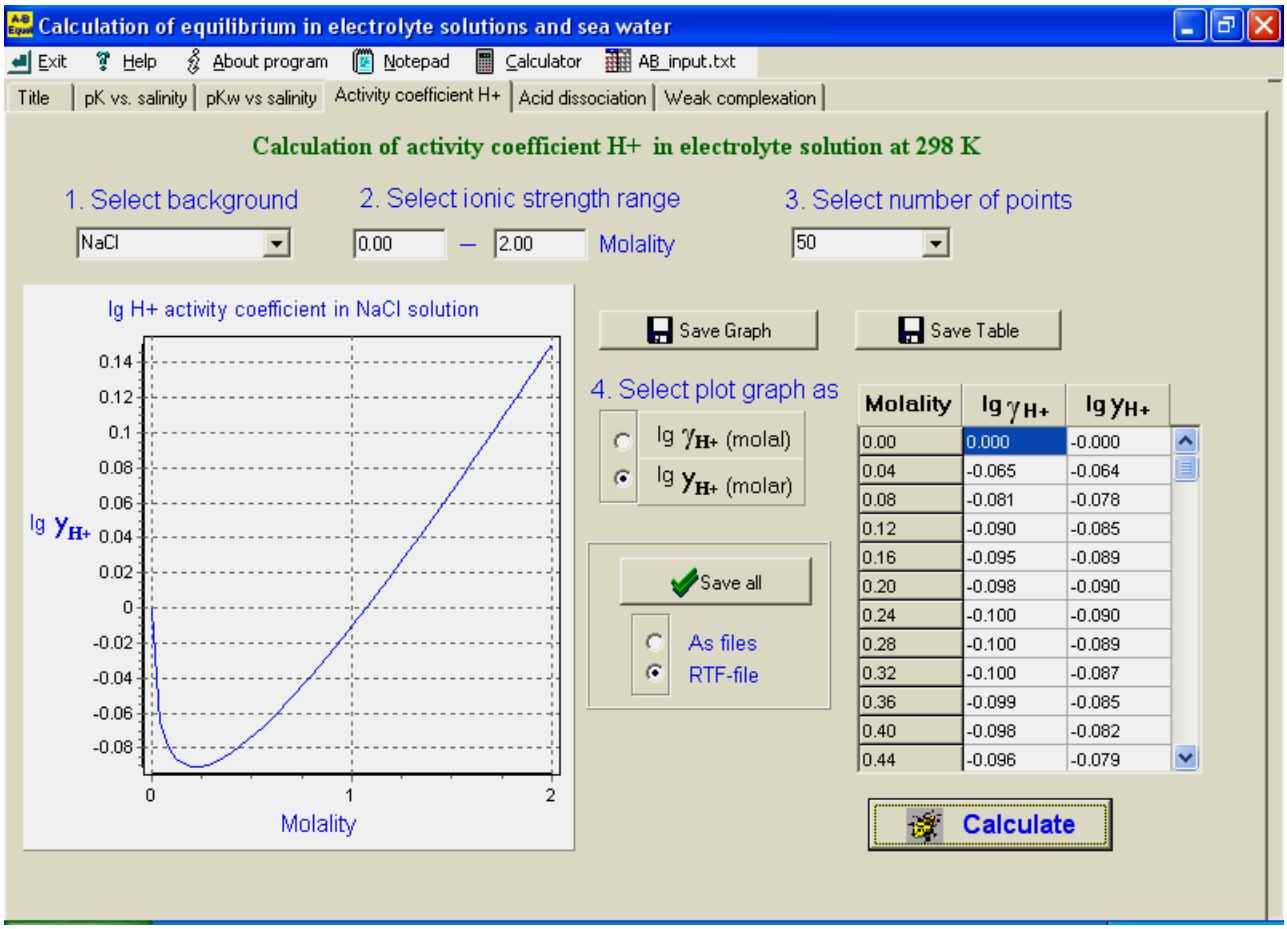
- Indicate the number of points
- Press the "  **Calculate**" button

It is possible to save

- the table of the calculated values as a text file (***.txt**) and to the clipboard simultaneously
- the plot as a graphic file (***.bmp**) and to the clipboard simultaneously
- all results together (table, plot, comments) in RTF format

Activity coefficient H^+

A 'Activity coefficient H^+' tabbed page is shown below



H^+ activity coefficient in electrolyte solutions is calculated by simplified Pitzer type equation [12]:

$$\ln \gamma_{H+} = f^{\gamma} + P \cdot I + Q \cdot I^2 + R \cdot I \cdot e^{-2\sqrt{I}} + T \cdot [1 - (1 + 2\sqrt{I})e^{-2\sqrt{I}}]$$

The molar – molal conversion is also performed.
Parameters of used equation are in the **AB_input.txt** file.

Calculate and save results

To calculate the H^+ activity coefficient in electrolyte solutions at 298 K

- Select background
- Select ionic strength range (from 0.0 to 2.0 molality)
- Indicate the number of points
- Indicate desired type of "**Plot graph as**"
- Press the "**Calculate**" button

Graphs may be plotted using the coordinates

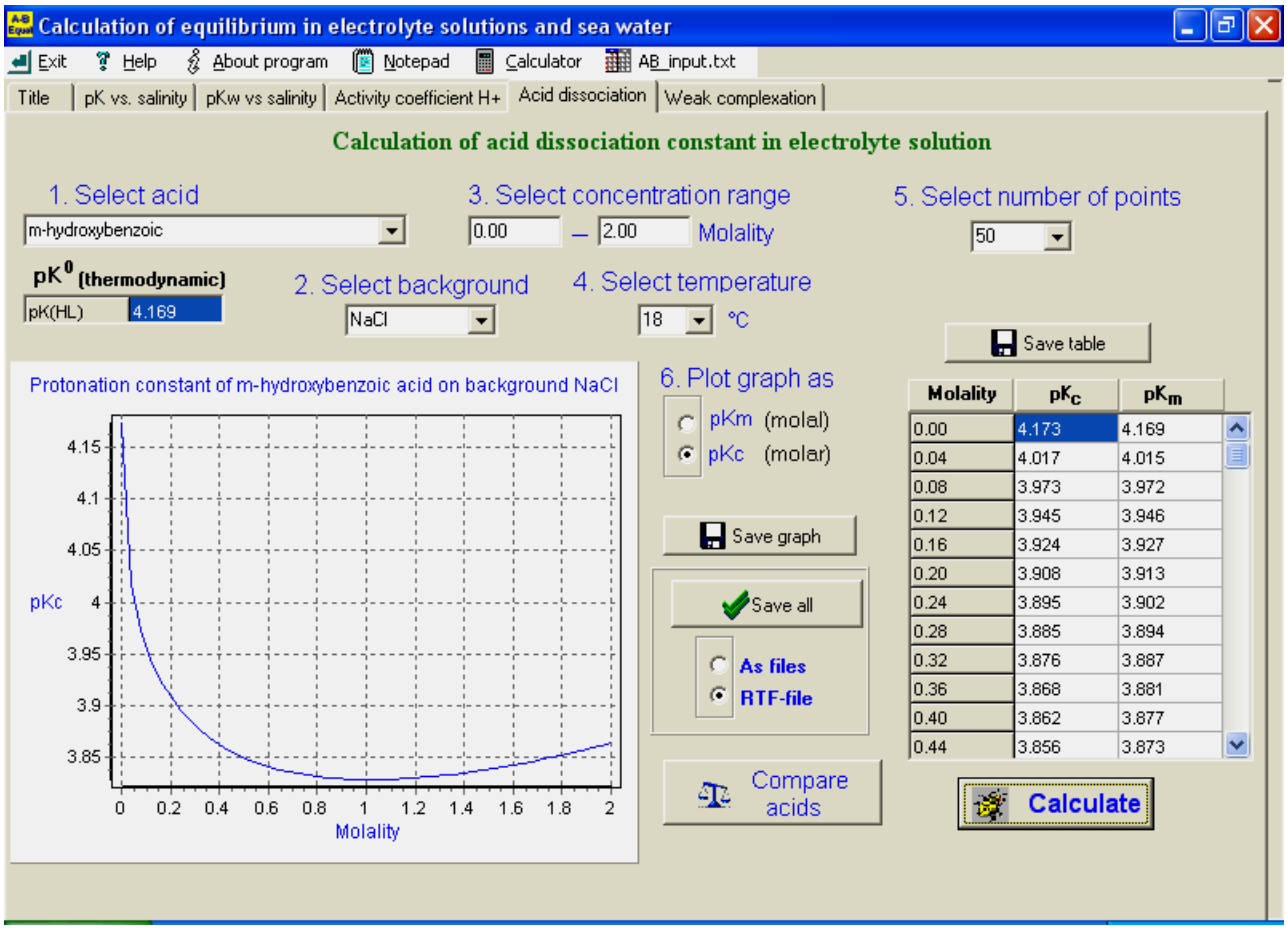
- lg γ_{H+} (molal)
- lg y_{H+} (molar)

It is possible to save

- the table of the calculated values as text file (***.txt**) and to a clipboard simultaneously
- the plot as a graphic file (***.bmp**) and to a clipboard simultaneously
- all results together (table, plot, comments) as a protocol in RTF format

Acid dissociation

A 'Acid dissociation' tabbed page is shown below



Dissociation constants of most common acids are calculated by the simplified Pitzer equation [13]:

$$pK_m^* = pK^T + \frac{2}{\ln 10} f^\gamma + \frac{2\beta^1_{MX}}{\ln 10} I e^{-2\sqrt{I}} + AI + B[1-(1+2\sqrt{I})e^{-2\sqrt{I}}]$$

Equation is adequate up to 2 mol/l ionic strength, thought it can be used to estimate.
Data for 25 °C and 18 °C for different electrolytes are included. Molal constants are used in above equation. The molal –molar conversion is also possible [14].
Parameters of equation are in the **AB_input.txt** file.

Calculate and save results

To calculate the acid dissociation constants

- Select acid from list
- Select background electrolyte
- Select concentration range
- Indicate the temperature (25 °C or 18 °C)
- Select the number of points
- Select desired type of "**Plot graph as**"
- Press the "**Calculate**" button

Graphs may be plotted using the coordinates

- pKm (molal)
- pKc (molar)

The user can save

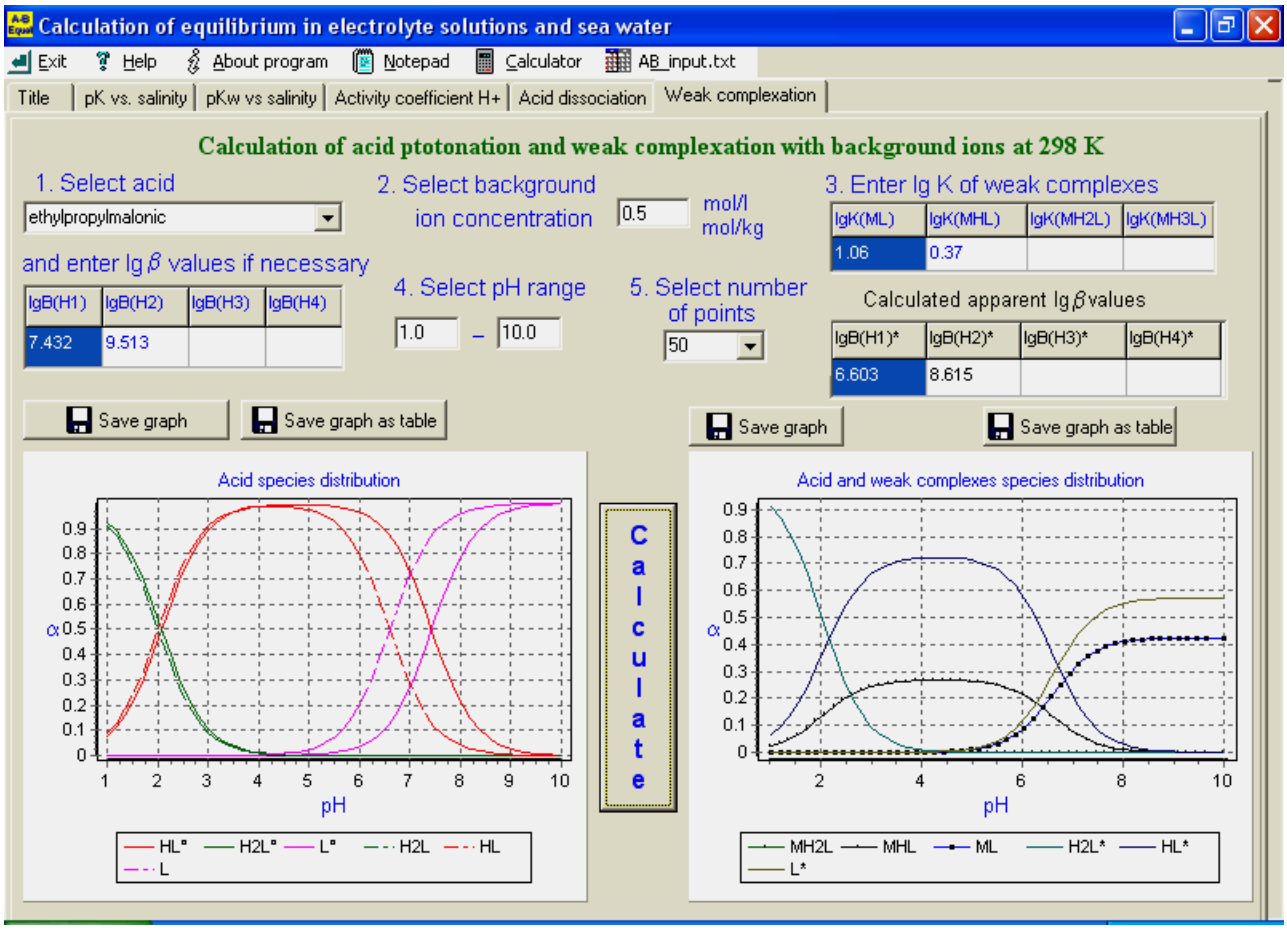
- the table of the calculated values as a text file (***.txt**) and to the clipboard simultaneously
- the plot as a graphic file (***.bmp**) and to the clipboard simultaneously
- all results together (table, plot, comments) in RTF format

The user can also compare

- acid dissociation constants from molality at selected temperature and background "**Compare acids**"

Weak complexation

A 'Weak complexation' tabbed page is shown below



Apparent overall protonation constants lgβ* are calculated. The apparent protonation constants lg β* differ from thermodynamic values lgβ^0 because of the complexation of acid ionic forms with the background ions. For example, for dissociation HA monocarboxylic acid in background Me^+An^-, pK*= lgβ* values are calculated as [15]

$$\mathbf{pK^* = pK^0 - lg(1 + K^{MeA}[Me^+])} \quad (*)$$

If the thermodynamic and apparent constants are known, it is possible to calculate the mole fractions of the ionic forms of acid and mole fractions of weak complexes with background ions [16]:

$$\frac{\sum j\beta_j^{\mathrm{H}}[\mathrm{H}]^j}{1+\sum \beta_j^{\mathrm{H}}[\mathrm{H}]^j} = \frac{\sum j\beta_j^{\mathrm{H}}[\mathrm{H}]^j + \sum q\beta_{pq}[\mathrm{H}]^q[\mathrm{B}]^p}{1+\sum \beta_j^{\mathrm{H}}[\mathrm{H}]^j + \sum \beta_{pq}[\mathrm{H}]^q[\mathrm{B}]^p}$$

Apparent protonation constants β_{pq} can be estimated by using the relationship (*) for generic equilibria

$$\mathrm{L} + p\mathrm{B} + q\mathrm{H} = \mathrm{B}_p L H_q$$

A lot of formation constant of weak complexes, details and methodology are in [17-35].

For user convenience the set of thermodynamic constants for above 250 acids is included in **AB_input** file [36].

Calculate and save results

To calculate the equilibria of acids and their weak complexes

- Select acid
- Select background ion concentration
- Enter lg K of weak complexes
- Select pH range
- Select the number of points
- Press the "**Calculate**" button

The user can save

- the table of the calculated values as a text file (***.txt**) and to the clipboard simultaneously
- the plot as a graphic file (***.bmp**) and to the clipboard simultaneously

The user can also

- Calculate the equilibrium molar fraction of ionic forms of polycarboxylic acids at different pH
- Calculate the equilibrium molar fraction of free ionic forms of polycarboxylic acids and the equilibrium molar fraction of weak complexes of ionic forms of polycarboxylic acids with ion background electrolyte at different pH

Input file

The **AB_input.txt** file contains parameters for tabbed pages
The below is example of input file:

```
---------------------------------------------------------------------
<pK vs. Salinity>
<name; thermodynamic constant lgKT;  a1;       a2;       a3; >
[acids] <acids>
acetic   4.75     -0.134  0.0213  -0.0015
malonic           5.70     -0.423  0.0561  -0.0027
         8.57     -0.550  0.0732  -0.0038
succinic          5.64     -0.297  0.0419  -0.0021
         9.85     -0.434  0.0631  -0.0036
malic    5.10     -0.301  0.0411  -0.0021
         8.57     -0.439  0.0652  -0.0038

[bases]  <bases>
ethylenediamine          9.91     0         0.003714         0
         6.86     0.1594  -0.01958         0.00114
diethylentriamine        9.80     0         0.003178         0
         8.74     0.1481  -0.01865         0.00114
         3.66     0.4452  -0.06523         0.00344
triethylenetetramine     9.67     0         -0.01211         0
         8.87     0.1756  -0.0201 0.00114
         6.12     0.3824  -0.06102         0.00344
         2.38     0.8332  -0.1675 0.01095
<---------------------------------------------------------------->
<Activity coefficient H+>
[Activity coefficient H+]
<background;     P;     Q;       R;       T;>

KBr      0.4020  -0.01363         0.2212  0.2458
KNO3     0.2338  0.0043  0.0494  0.2959
KCl      0.3650  -0.0062 0.2122  0.1884
<---------------------------------------------------------------->

<Acid Dissociation>
[Acid and base dissociation]
<acid name; background; thermodynamic constant pKT; A and B Pitzer parameters;>

{25} <temperature: 25 C>
acetic   KNO3  4.78     0.18     0.22
         KCl      4.78     0.223    0.221
         NaCl     4.78     0.224    0.168
         NaNO3 4.78     0.167    0.274
benzoic  KNO3  4.21     0.13     0.35
cloroacetic      KNO3  2.84     0.14     0.37
formic   NaCl     3.752    0.210    0.151
         KCl      3.752    0.221    0.204
         KNO3  3.752    0.160    0.330
         NaNO3 3.752    0.151    0.258

{18} <temperature: 18 C>
acetic   NaCl     4.777    0.228    0.126
         KCl      4.774    0.225    0.189
formic   NaCl     3.750    0.216    0.123
```

```
          KCl     3.750   0.215   0.205
propionic         NaCl    4.878   0.218   0.166
          KCl     4.888   0.218   0.212

<---------------------------------------------------------------->

[Conversion to molar scale]
<Conversion to molar scale, used equation ro=a*molal+0.998, ro=molal/molar>
<background; molar weight; a-factor;>

NaCl    58.44   0.0214
NaClO4          122.44  0.0485
NaNO3 84.99     0.0341
NaBr    102.89  0.0283
KBr     119.00  0.0350
KCl     74.55   0.0322
KNO3    101.10  0.043
<---------------------------------------------------------------->

<Weak complexation>
[Weak complexation] <298.15 K>
<acid   K1      K2      K3      K4>
formic  1.835e-4
acetic  1.780e-5
propionic         1.343e-5
n-butyric         1.508e-5
valeric  1.38e-5
caproic 1.255e-5
enanthic          1.28e-5
caprylic          1.28e-5
pelargonic        1.11e-5
isobutyric        1.374e-5
isovaleric        1.657e-5
acrylic  5.55e-5
-----------------------------------------------------------------------------------------------------------
-----------------------------------------------------------------------------------------------------------
```

The user can edit and add to the input file. Note that the columns need only be separated by tab (→|). Comments may be interspersed freely within the data files provided they are contained between angle brackets < >.

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