Data Mining. 1.
Glycine Content Estimation from Activity Coefficients Measurement

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Abstract

The paper presents a method to estimate the glycine content from salt aqueous solutions based on standard adding of salt repeated activity coefficients measurement. An original program for data mining is presented. The program execution shows that the glycine content can be predicted from mean ionic activity coefficients in the presence of glycine at room chamber temperature.

The original program was build up on PHP technology and can run via HTTP service at the address:

http://academicdirect.ro/virtual_library/molecular_topology/data_mining/

Keywords

Data mining, PHP programming, QSPR/QSAR studies

Introduction

The software market provides a varied offer for data mining and analysis. Beginning with office software like Microsoft Excel [1] and ending with professional data mining software like StatSoft Statistica [2] a large list of choices and modalities to mining data are available. Even if the software pool is sometimes endless, it does not offer a complete answer on data dependency. In a previous paper [3], it was discussed a program capable to consider all possible dependencies in a data set and to generate a complete list of data predictors. The program was adapted now to store results into a database; by querying the database is now possible to obtain the best predictor of selected variable.

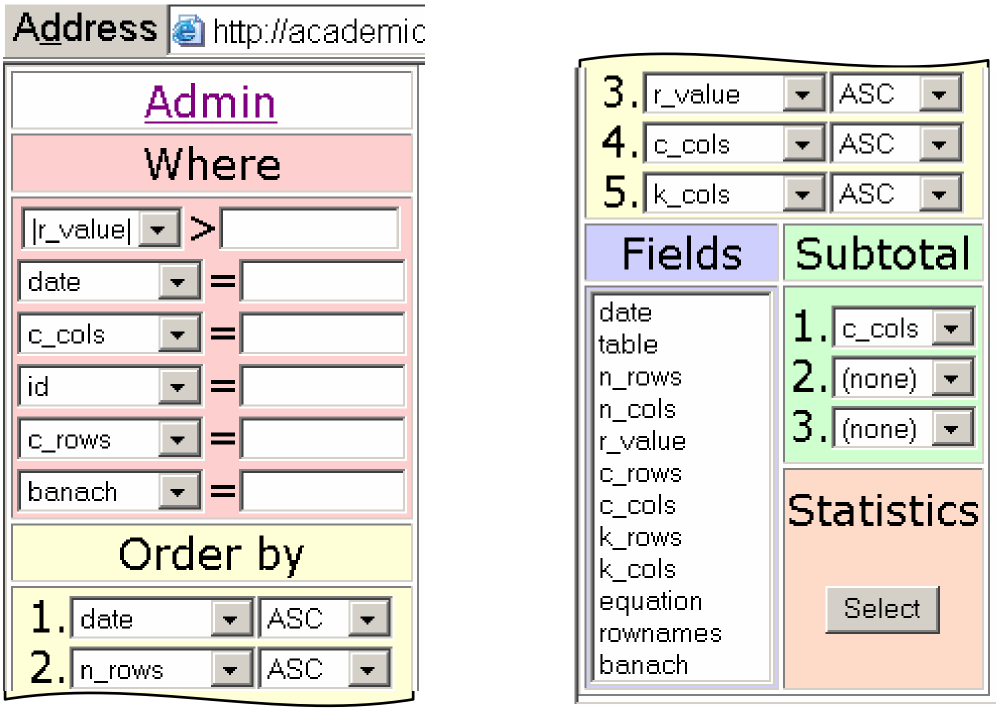
Note that the actual program does not replace the old one in tasks. First, located at the address

http://vl.academicdirect.ro/applied_statistics/linear_regression/multiple/v1.5/

it makes all recursively combinations to find dependencies. The present one considers only a user selection subset of the data set, the results being used for prediction, validation and comparison.

Program Interface and Architecture

The program has two interfaces: the first one (figure 1) is for query statistics and allows user to enounce a SQL query for `statistics` table interrogation.



Address http://academic

Where
|r_value| >
date =
c_cols =
id =
c_rows =
banach =

Order by
1. date ASC
2. n_rows ASC
3. r_value ASC
4. c_cols ASC
5. k_cols ASC

Fields
date
table
n_rows
n_cols
r_value
c_rows
c_cols
k_rows
k_cols
equation
rownames
banach

Subtotal
1. c_cols
2. (none)
3. (none)

Fig. 1. Query statistics menu of data_mining program

First, the user selects his fields and the order (by clauses) of subtotal statistics, by pressing the Select button; the query is thus made.

The second menu interface is available from Admin link and leads to (figure 2):

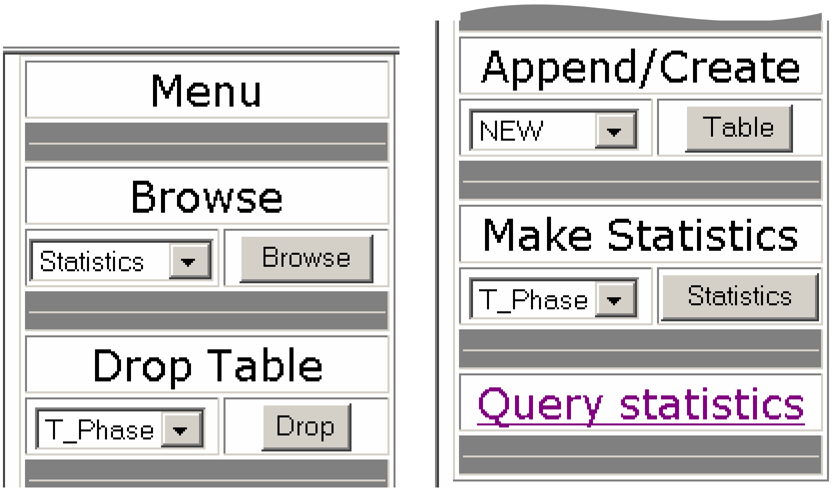


Fig. 2. Operations menu of the data mining program

Note that the access to the operations menu is password restricted, by data security reasons. First step of data analysis is *data submitting* to server, via append/create option (figure 3):

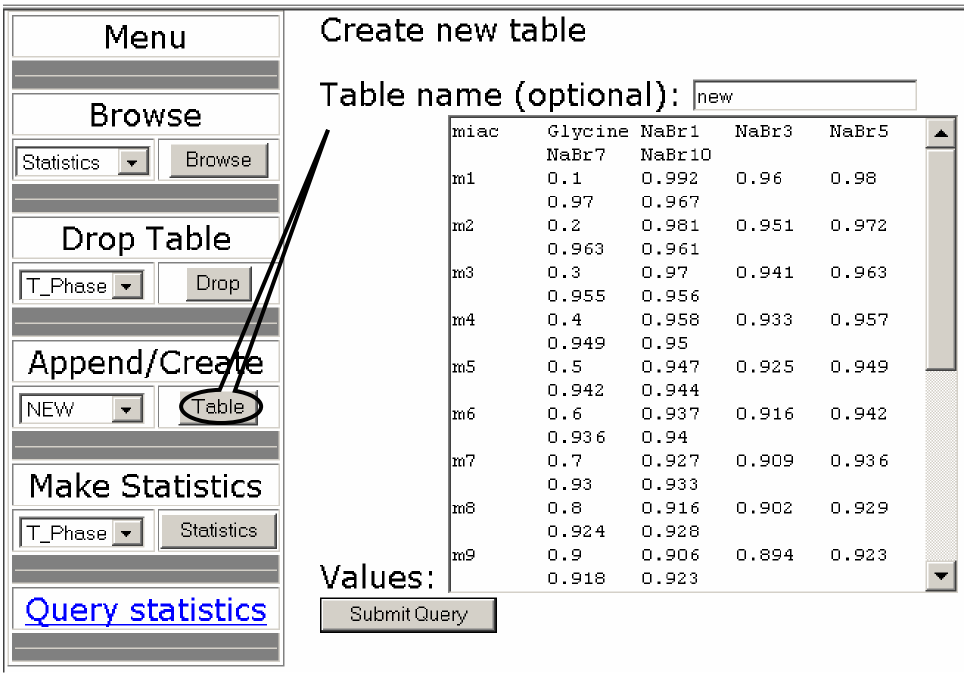


Table name (optional): new

Values:

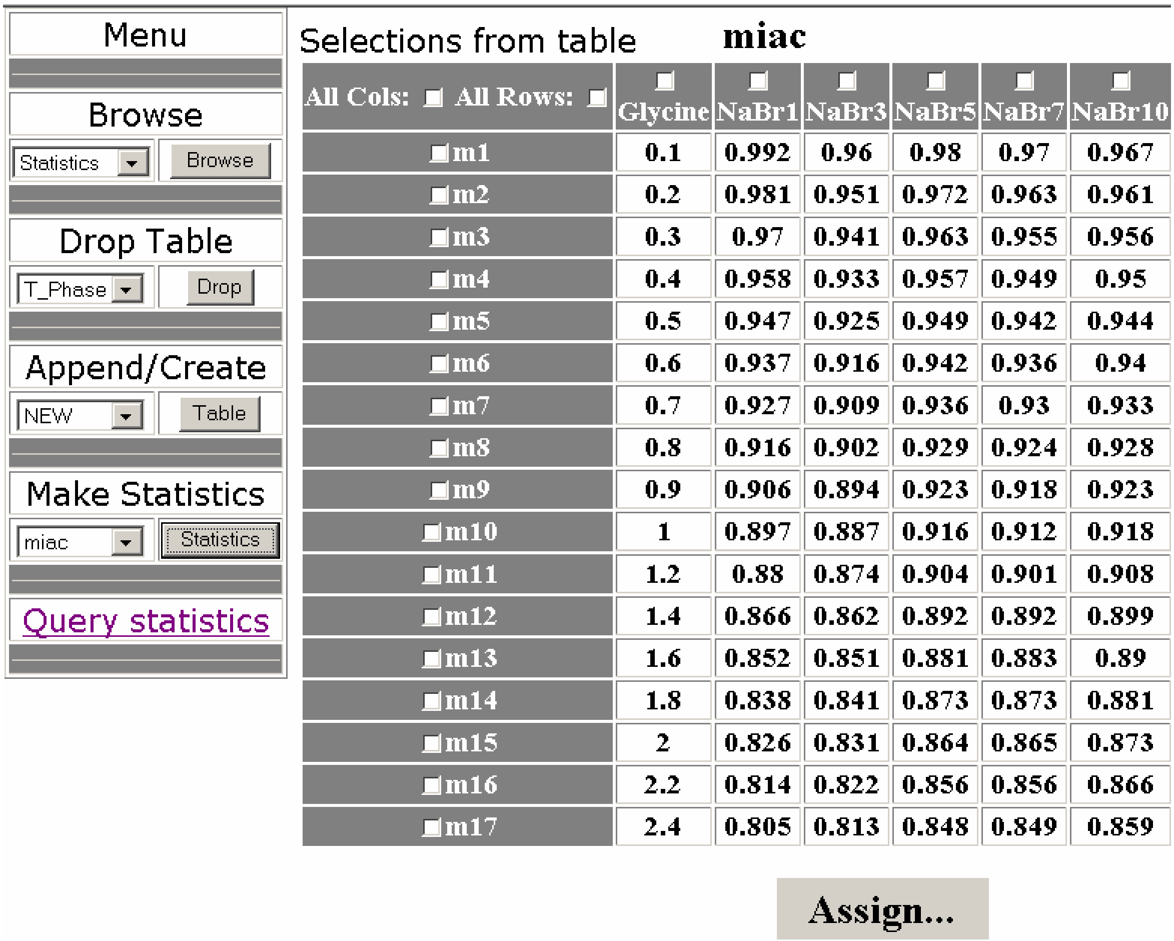
```
miac    Glycine NaBr1   NaBr3   NaBr5
        NaBr7   NaBr10
m1      0.1     0.992   0.96    0.98
        0.97    0.967
m2      0.2     0.981   0.951   0.972
        0.963   0.961
m3      0.3     0.97    0.941   0.963
        0.955   0.956
m4      0.4     0.958   0.933   0.957
        0.949   0.95
m5      0.5     0.947   0.925   0.949
        0.942   0.944
m6      0.6     0.937   0.916   0.942
        0.936   0.94
m7      0.7     0.927   0.909   0.936
        0.93    0.933
m8      0.8     0.916   0.902   0.929
        0.924   0.928
m9      0.9     0.906   0.894   0.923
        0.918   0.923
```

Fig. 3. Data uploading (data_mining program)

The data must be in table format, with columns, rows and captions included. The submitted data are stored into a MySQL table with the same names as gives by the user.

After uploading, the table will appear in table's lists. The user can browse or drop the table and, most important, can make statistics on it.

First step in statistics making is to select a subset of data (figure 4).

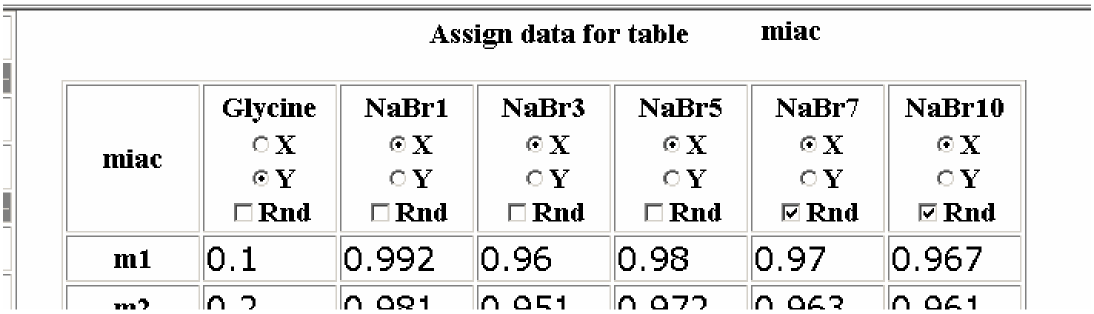


Selections from table **miac**

All Cols: □ All Rows: □	□ Glycine	□ NaBr1	□ NaBr3	□ NaBr5	□ NaBr7	□ NaBr10
□m1	0.1	0.992	0.96	0.98	0.97	0.967
□m2	0.2	0.981	0.951	0.972	0.963	0.961
□m3	0.3	0.97	0.941	0.963	0.955	0.956
□m4	0.4	0.958	0.933	0.957	0.949	0.95
□m5	0.5	0.947	0.925	0.949	0.942	0.944
□m6	0.6	0.937	0.916	0.942	0.936	0.94
□m7	0.7	0.927	0.909	0.936	0.93	0.933
□m8	0.8	0.916	0.902	0.929	0.924	0.928
□m9	0.9	0.906	0.894	0.923	0.918	0.923
□m10	1	0.897	0.887	0.916	0.912	0.918
□m11	1.2	0.88	0.874	0.904	0.901	0.908
□m12	1.4	0.866	0.862	0.892	0.892	0.899
□m13	1.6	0.852	0.851	0.881	0.883	0.89
□m14	1.8	0.838	0.841	0.873	0.873	0.881
□m15	2	0.826	0.831	0.864	0.865	0.873
□m16	2.2	0.814	0.822	0.856	0.856	0.866
□m17	2.4	0.805	0.813	0.848	0.849	0.859

Fig. 4. Data selecting (*data_mining program*)

Based on user selection, the program displays selected values (figure 5) and allows user to select the dependent and independent variables (X for independent, Y for dependent ones). Further, *Rnd check box* enables, for the selected variable(s), a test of significance or validation, by permuting values into a column.

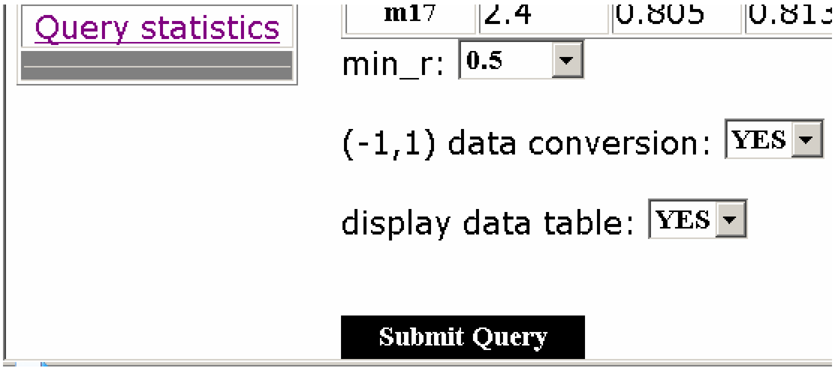


Assign data for table miac

miac	Glycine ○ X ● Y □ Rnd	NaBr1 ● X ○ Y □ Rnd	NaBr3 ● X ○ Y □ Rnd	NaBr5 ● X ○ Y □ Rnd	NaBr7 ● X ○ Y ☑ Rnd	NaBr10 ● X ○ Y ☑ Rnd
m1	0.1	0.992	0.96	0.98	0.97	0.967
m2	0.2	0.981	0.951	0.972	0.963	0.961

Fig. 5. Data assigning (data_mining program)

In the same window (figure 6), after the data assignment, the user must select the required threshold for the correlation coefficient *r*. If the user wants to convert the data to a Banach Space [4], he submits them to the partial least squares coefficients determination procedure [5].



Query statistics

m17	2.4	0.805	0.81

min_r: 0.5

(-1,1) data conversion: YES

display data table: YES

Fig. 6. Limits and conversion features (*data_mining program*)

All statistics results are written into a `statistics` table with the structure given below.

c_cols	date	table	n_rows	n_cols	r_value	c_rows	k_rows	k_cols	equation	rownames	banach	id

In the above, `c_cols` column stores the name of permuted values column (if any) or "Y" value otherwise and allows to select a specific subset of correlation data, according to the permuted column (*Rnd* option). The `date` column stores the date in format YY:MM:DD:HH:mm:SS (Y-year, M-month, D-day, H-hour, m-minute, S-second, *e.g.*, 03:10:01:18:13:49). The `table` column stores the name of original table, from which a subset was extracted. The `n_rows` and `n_cols` store the number of data rows and columns (excepting the subtotal records, for which the fields is empty). The `r_value` column stores the correlation coefficient founds. The `c_rows` contain the name of starting row in rows permutation (if any), empty (for subtotals) or null (for non-permuted data). The `k_rows` contain an ordered list of all considered rows, stored by their record numbers. The `k_cols` is the place for selected columns. The `equation` field contains the regression equation as a string (in our case, a value is given in eq. 1. The `rownames` field stores an ordered list of names for selected rows. Finally, the `banach` field can store only two values (0 or 1), depending on user choice, about the converting data to a Banach Space.

Results and discussion

Using the data_mining program it is easy to discover the dependency between measured or calculated parameters. A set of experimental data [6] (Table 1) was considered for testing the program. The collected data represent the ratio of the mean ionic activity coefficients of NaBr, in the presence of glycine, at different NaBr and glycine molalities, at T = 298.15 K. The NaBrX (X=1, 3, 5, 7, 10) columns contain the activity coeffcients of NaBr solved in ratios of 0.1, 0.3, 0.5, 0.7 and 1.0 mol·kg^{-1}. For glycine, only molality (in I.S. units) is provided.

Table 1. Ratios of the mean ionic activity coefficients of NaBr in the presence of glycine [6]

miac	Glycine	NaBr1	NaBr3	NaBr5	NaBr7	NaBr10
m1	0.1	0.992	0.96	0.98	0.97	0.967
m2	0.2	0.981	0.951	0.972	0.963	0.961
m3	0.3	0.97	0.941	0.963	0.955	0.956
m4	0.4	0.958	0.933	0.957	0.949	0.95
m5	0.5	0.947	0.925	0.949	0.942	0.944
m6	0.6	0.937	0.916	0.942	0.936	0.94
m7	0.7	0.927	0.909	0.936	0.93	0.933
m8	0.8	0.916	0.902	0.929	0.924	0.928
m9	0.9	0.906	0.894	0.923	0.918	0.923
m10	1	0.897	0.887	0.916	0.912	0.918
m11	1.2	0.88	0.874	0.904	0.901	0.908
m12	1.4	0.866	0.862	0.892	0.892	0.899
m13	1.6	0.852	0.851	0.881	0.883	0.89
m14	1.8	0.838	0.841	0.873	0.873	0.881
m15	2	0.826	0.831	0.864	0.865	0.873
m16	2.2	0.814	0.822	0.856	0.856	0.866
m17	2.4	0.805	0.813	0.848	0.849	0.859

The query of `statistics` table on all `miac` selected values shows that the glycine concentration is strongly dependent on NaBr ionic activity (if both exists in solution). The equation that proves this truth is:

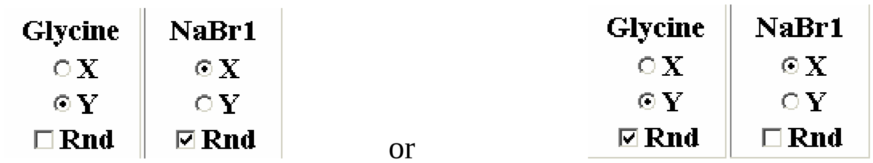
$$Y_{Glycine}=21.448X_{NaBr1}-0.232X_{NaBr3}-22.943X_{NaBr5}-27.755X_{NaBr7}+7.884X_{NaBr10}+20.808*1$$

$$m = 17;\ r = 0.998 \qquad (1)$$

The program allows the calculation of monovariate regression (i.e., a single independent variable, *e.g.*, NaBr1):

$$Y_{Glycine}=-11.977*X_{NaBr1}+11.853*1$$
$$m = 17;\ r = 0.992 \qquad (2)$$

Supposing that we want to validate the assumption of NaBr1 dependency, all that we have to do is to include a validation test on NaBr1 variable in our program. This task can be done on two ways (figure 7).



Glycine	NaBr1
○X	●X
●Y	○Y
□Rnd	☑Rnd

or

Glycine	NaBr1
○X	●X
●Y	○Y
☑Rnd	□Rnd

Fig. 7. Validation test running (Rnd checkbox selection)

The execution of the program in both cases will produce a set of correlations (figure 8, see also figure 7 for correspondences):

$Y_{Glycine}=-11.9774*X_{NaBr1}+11.8528*1$ r=0.9921	$Y_{Glycine}=-11.9774*X_{NaBr1}+11.8528*1$ r=0.9921
$Y_{Glycine}=-7.4288*X_{NaBr1}+7.7558*1$ r=0.6153 X_{NaBr1}->m2	$Y_{Glycine}=-8.5594*X_{NaBr1}+8.7742*1$ r=0.709 $Y_{Glycine}$->m2
$Y_{Glycine}=-3.5341*X_{NaBr1}+4.2479*1$ r=0.2927 X_{NaBr1}->m3	$Y_{Glycine}=-5.3571*X_{NaBr1}+5.8899*1$ r=0.4437 $Y_{Glycine}$->m3
$Y_{Glycine}=-0.2988*X_{NaBr1}+1.3338*1$ r=0.0247 X_{NaBr1}->m4	$Y_{Glycine}=-2.4992*X_{NaBr1}+3.3157*1$ r=0.207 $Y_{Glycine}$->m4
$Y_{Glycine}=2.2304*X_{NaBr1}-0.9442*1$ r=0.1847 X_{NaBr1}->m5	$Y_{Glycine}=0.0126*X_{NaBr1}+1.0534*1$ r=0.001 $Y_{Glycine}$->m5
$Y_{Glycine}=4.0916*X_{NaBr1}-2.6206*1$ r=0.3389 X_{NaBr1}->m6	$Y_{Glycine}=2.0877*X_{NaBr1}-0.8157*1$ r=0.1729 $Y_{Glycine}$->m6
$Y_{Glycine}=5.3249*X_{NaBr1}-3.7314*1$ r=0.441 X_{NaBr1}->m7	$Y_{Glycine}=3.7193*X_{NaBr1}-2.2853*1$ r=0.308 $Y_{Glycine}$->m7
$Y_{Glycine}=5.9267*X_{NaBr1}-4.2735*1$ r=0.4909 X_{NaBr1}->m8	$Y_{Glycine}=4.9022*X_{NaBr1}-3.3507*1$ r=0.406 $Y_{Glycine}$->m8
$Y_{Glycine}=5.8571*X_{NaBr1}-4.2108*1$ r=0.4851 X_{NaBr1}->m9	$Y_{Glycine}=5.5023*X_{NaBr1}-3.8912*1$ r=0.4557 $Y_{Glycine}$->m9

Fig. 8. Output of validation tests

$Y_{Glycine}$=5.5023*X_{NaBr1}-3.8912*1
r=0.4557 X_{NaBr1}->m10

$Y_{Glycine}$=4.9022*X_{NaBr1}-3.3507*1
r=0.406 X_{NaBr1}->m11

$Y_{Glycine}$=3.7193*X_{NaBr1}-2.2853*1
r=0.308 X_{NaBr1}->m12

$Y_{Glycine}$=2.0877*X_{NaBr1}-0.8157*1
r=0.1729 X_{NaBr1}->m13

$Y_{Glycine}$=0.0126*X_{NaBr1}+1.0534*1
r=0.001 X_{NaBr1}->m14

$Y_{Glycine}$=-2.4992*X_{NaBr1}+3.3157*1
r=0.207 X_{NaBr1}->m15

$Y_{Glycine}$=-5.3571*X_{NaBr1}+5.8899*1
r=0.4437 X_{NaBr1}->m16

$Y_{Glycine}$=-8.5594*X_{NaBr1}+8.7742*1
r=0.709 X_{NaBr1}->m17

$Y_{Glycine}$=-11.9774*X_{NaBr1}+11.8528*1
r=0.9921 X_{NaBr1}->m1

$Y_{Glycine}$=5.8571*X_{NaBr1}-4.2108*1
r=0.4851 $Y_{Glycine}$->m10

$Y_{Glycine}$=5.9267*X_{NaBr1}-4.2735*1
r=0.4909 $Y_{Glycine}$->m11

$Y_{Glycine}$=5.3249*X_{NaBr1}-3.7314*1
r=0.441 $Y_{Glycine}$->m12

$Y_{Glycine}$=4.0916*X_{NaBr1}-2.6206*1
r=0.3389 $Y_{Glycine}$->m13

$Y_{Glycine}$=2.2304*X_{NaBr1}-0.9442*1
r=0.1847 $Y_{Glycine}$->m14

$Y_{Glycine}$=-0.2988*X_{NaBr1}+1.3338*1
r=0.0247 $Y_{Glycine}$->m15

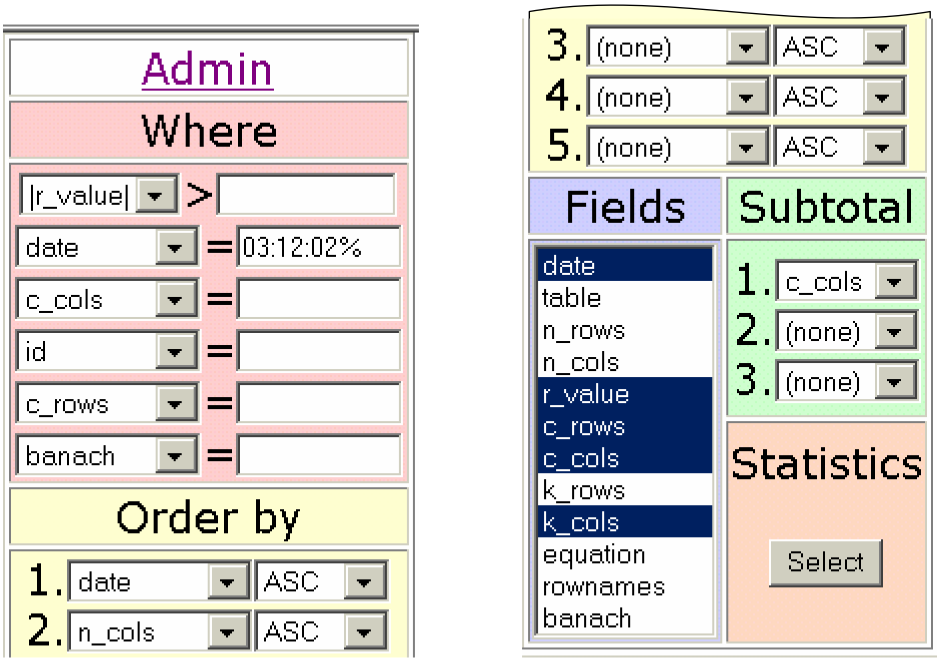
$Y_{Glycine}$=-3.5341*X_{NaBr1}+4.2479*1
r=0.2927 $Y_{Glycine}$->m16

$Y_{Glycine}$=-7.4288*X_{NaBr1}+7.7558*1
r=0.6153 $Y_{Glycine}$->m17

$Y_{Glycine}$=-11.9774*X_{NaBr1}+11.8528*1
r=0.9921 $Y_{Glycine}$->m1

Fig. 8. Output of validation tests (continuing)

After the regression validation procedure running, the program put automatically the regression results into the database. A query can be applied now to the database (see also fig 1):



Admin

Where

|r_value| >
date = 03:12:02%
c_cols =
id =
c_rows =
banach =

Order by

1. date ASC
2. n_cols ASC
3. (none) ASC
4. (none) ASC
5. (none) ASC

Fields

date
table
n_rows
n_cols
r_value
c_rows
c_cols
k_rows
k_cols
equation
rownames
banach

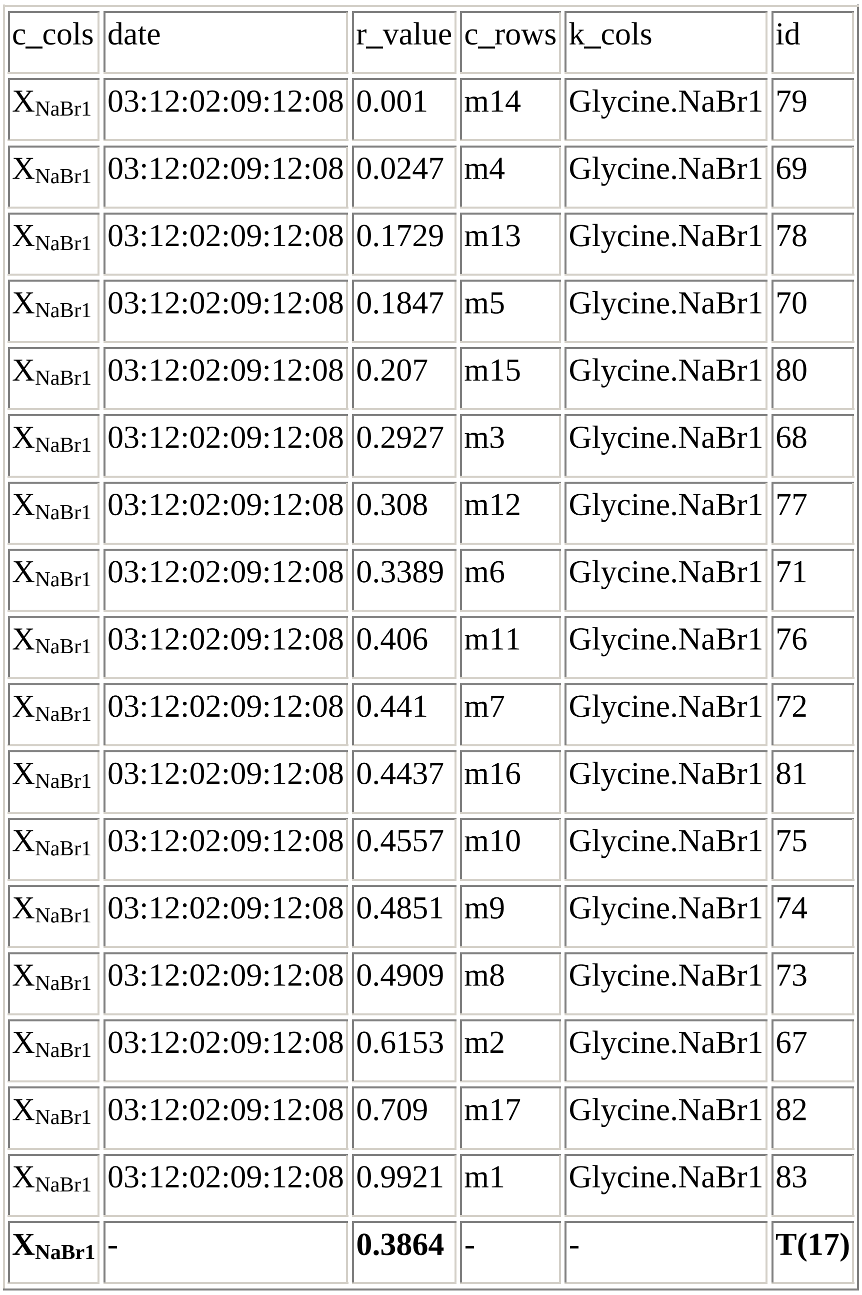
Subtotal

1. c_cols
2. (none)
3. (none)

Statistics

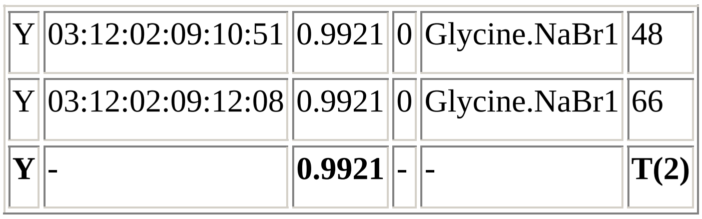
Fig. 9. Query statistics for validation analysis

The query from figure 9 will produce a full analysis of database contents, detailed in figure 10 (a, b and c):



c_cols	date	r_value	c_rows	k_cols	id
X_{NaBr1}	03:12:02:09:12:08	0.001	m14	Glycine.NaBr1	79
X_{NaBr1}	03:12:02:09:12:08	0.0247	m4	Glycine.NaBr1	69
X_{NaBr1}	03:12:02:09:12:08	0.1729	m13	Glycine.NaBr1	78
X_{NaBr1}	03:12:02:09:12:08	0.1847	m5	Glycine.NaBr1	70
X_{NaBr1}	03:12:02:09:12:08	0.207	m15	Glycine.NaBr1	80
X_{NaBr1}	03:12:02:09:12:08	0.2927	m3	Glycine.NaBr1	68
X_{NaBr1}	03:12:02:09:12:08	0.308	m12	Glycine.NaBr1	77
X_{NaBr1}	03:12:02:09:12:08	0.3389	m6	Glycine.NaBr1	71
X_{NaBr1}	03:12:02:09:12:08	0.406	m11	Glycine.NaBr1	76
X_{NaBr1}	03:12:02:09:12:08	0.441	m7	Glycine.NaBr1	72
X_{NaBr1}	03:12:02:09:12:08	0.4437	m16	Glycine.NaBr1	81
X_{NaBr1}	03:12:02:09:12:08	0.4557	m10	Glycine.NaBr1	75
X_{NaBr1}	03:12:02:09:12:08	0.4851	m9	Glycine.NaBr1	74
X_{NaBr1}	03:12:02:09:12:08	0.4909	m8	Glycine.NaBr1	73
X_{NaBr1}	03:12:02:09:12:08	0.6153	m2	Glycine.NaBr1	67
X_{NaBr1}	03:12:02:09:12:08	0.709	m17	Glycine.NaBr1	82
X_{NaBr1}	03:12:02:09:12:08	0.9921	m1	Glycine.NaBr1	83
X_{NaBr1}	-	**0.3864**	-	-	**T(17)**

Fig. 10. (a) Validation statistics for X randomizing (see fig. 7)



Y	03:12:02:09:10:51	0.9921	0	Glycine.NaBr1	48
Y	03:12:02:09:12:08	0.9921	0	Glycine.NaBr1	66
Y	-	**0.9921**	-	-	**T(2)**

Fig. 10. (b) Validation statistics without randomizing (continuing from figure 10a)

$Y_{Glycine}$	03:12:02:09:10:51	0.001	m5	Glycine.NaBr1	52
$Y_{Glycine}$	03:12:02:09:10:51	0.0247	m15	Glycine.NaBr1	62
$Y_{Glycine}$	03:12:02:09:10:51	0.1729	m6	Glycine.NaBr1	53
$Y_{Glycine}$	03:12:02:09:10:51	0.1847	m14	Glycine.NaBr1	61
$Y_{Glycine}$	03:12:02:09:10:51	0.207	m4	Glycine.NaBr1	51
$Y_{Glycine}$	03:12:02:09:10:51	0.2927	m16	Glycine.NaBr1	63
$Y_{Glycine}$	03:12:02:09:10:51	0.308	m7	Glycine.NaBr1	54
$Y_{Glycine}$	03:12:02:09:10:51	0.3389	m13	Glycine.NaBr1	60
$Y_{Glycine}$	03:12:02:09:10:51	0.406	m8	Glycine.NaBr1	55
$Y_{Glycine}$	03:12:02:09:10:51	0.441	m12	Glycine.NaBr1	59
$Y_{Glycine}$	03:12:02:09:10:51	0.4437	m3	Glycine.NaBr1	50
$Y_{Glycine}$	03:12:02:09:10:51	0.4557	m9	Glycine.NaBr1	56
$Y_{Glycine}$	03:12:02:09:10:51	0.4851	m10	Glycine.NaBr1	57
$Y_{Glycine}$	03:12:02:09:10:51	0.4909	m11	Glycine.NaBr1	58
$Y_{Glycine}$	03:12:02:09:10:51	0.6153	m17	Glycine.NaBr1	64
$Y_{Glycine}$	03:12:02:09:10:51	0.709	m2	Glycine.NaBr1	49
$Y_{Glycine}$	03:12:02:09:10:51	0.9921	m1	Glycine.NaBr1	65
$Y_{Glycine}$	-	**0.3864**	-	-	**T(17)**

Fig. 10 (c) Validation statistics for Y randomizing (see fig. 7, continuing from figure 10b)

Starting from ionic activity determinations in an unknown glycine concentration solution, a simple regression analysis provides a QSPR (quantitative structure- property relationship) model (eqs 1 or 2). The glycine concentration was determined with two decimals precision in NaBr+Glycine solutions.

The linear dependency between ionic activity and glycine concentration, given by eq 2, can be extended to solutions with unknown concentration of a significant component (say, aminoacid). The experimental part for ionic determination, according to [6], was performed on a Jenway ion analyzer, Model 3045.

Conclusions

The program allows an efficient management of data submitted to a correlation study, with re-viewing and differently selecting subsets.

The multiple subsets selection from inputted data let us to establish more than one QSPR/QSAR relations between data sets, depending on theoretical and/or experimental requests. The friendly interface of data analysis shorts significant the analysis time.

The results storage and data conversion features show the versatility and efficiency of the proposed data mining procedure.

References

The program:

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