Package **AquaEnv**: an Aquatic modelling Environment in **R**

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Abstract

AquaEnv is an integrated development toolbox for aquatic chemical model generation focused on (ocean) acidification and CO2 air-water exchange.

- It contains all elements necessary to model the pH, the related CO2 air-water exchange, as well as aquatic acid-base chemistry in general for an arbitrary marine, estuarine or freshwater system. Also chemical batches can be modelled.
- Next to the routines necessary to calculate desired information, AquaEnv also contains a suite of tools to visualize this information.
- Furthermore, AquaEnv can not only be used to build dynamic models of aquatic systems, but it can also serve as a simple desktop tool for the experimental aquatic chemist to generate and visualize all possible derived information from a set of measurements with one single easy to use R function.
- Additionally, the sensitivity of the system to variations in the input variables can be visualized.
- AquaEnv also contains a number of example "applications" that make use of the aquatic modelling toolbox that AquaEnv provides:
  - a theoretical titration simulator
  - and a routine to determine total alkalinity ([TA]), the total dissolved inorganic carbon concentration ([$\sum$CO2]), as well as additionally the electrode standard potential (E_0) and the first dissociation constant of the carbonate system ($K^*_{CO_2}$)

Keywords: aquatic modelling, pH, pH scales, dissolved inorganic carbon, total alkalinity, total alkalinity curve fitting, theoretical titration, revelle factor, omega, solubility products, CO_2, ocean acidification, estuaries, carbonate system, seawater, R.

Contents

1 Introduction

AquaEnvis a toolbox for aquatic modelling that serves several purposes

- It provides functions to calculate the stoichiometric equilibrium constants (K^*) for key acid base systems in natural seawater, the Henry's constants (K_0), as well as the solubility products (K_{sp}) for calcite and aragonite. This functionality is provided via the functions `K_CO2, K_HCO3, K_BOH3, K_W, K_HSO4, K_HF, K_NH4, K_H2S, K_H3PO4, K_H2PO4, K_HPO4, K_SiOH4, K_SiOOH3, K0_CO2, K0_O2, Ksp_aragonite,` and `Ksp_calcite`.

- all information (which information: including revelle, full speciation, all partial derivatives of ta needed for Hofmann, Meysman, Soetaert, and Middelburg (2008a) and ionization fractions as defined by Stumm and Morgan (1996) and used in Hofmann, Middelburg, Soetaert, Wolf-Gladrow, and Meysman (2008b) that can be calculated from all that is know over one single sample (tool for the experimentalist). this is done by the central function aquaenv. (is returnded as object of class aquaenv) Input for aquaenv has to be supplied in standard SI units and in molinity (mol/kg-solution) (footnote: explain importance of molinity vs molality), This can be done with the function convert.

  the information created with aquaenv is also supplied in standard SI units and in molinity and can be converted to other units with the function convert

  from any of the variable pairs .... also $\sum CO_2$ can be calculated

  one can use input vectors of T, S or d for aquaenv to obtain vectors of all possibly calculated information as function of the input vector this can be visualized in a large variety of ways using the plot function specially defined for objects of type aquaenv

  objects of class aquaenv can be used in dynamic models to define the state of the system in each timestep of the numerical integration (done e.g. with **deSolve**). with the function from.dataframe it is possible to convert output of those dynamic models into objects of type aquaenv which allows the user to use the whole suite of visualisation tools that is provided in AquaEnv.

  Hofmann *et al.* (2008a) and Hofmann *et al.* (2008b) describe methods for an "explicit" pH modelling which allows for the quantification of the influences of kinetically modelled processes on the pH. Objects of type aquaenv provide all needed quantities (partial derivatives of TA, ionization fractions) to employ both of those methods in dynamic models. Furthermore, **AquaEnv**provides the functionality to cumulatively plot the obtained influences on the pH.

  as an example of how to use the toolbox that is **AquaEnv**, two applications are provided

  the creation of theoretical titrations which can be used e.g. to create bjerrum plots, something that can also be done with the plot function in **AquaEnv**.

  a routine based on a method in DOE (1994) that makes use of that theoretical titration function and allows for determining total alkalinity ([TA]), the total dissolved inorganic carbon concentration ([$\sum$CO2]), as well as additionally the electrode standard potential (E_0) and the first dissociation constant of the carbonate system ($K^*_{CO_2}$) using the Levenberg-Marquart algorithm (least squares optimization procedure) as provided in **minpack.lm**

2 Using AquaEnv

2.1 Basic features

2.1.1 calling the "K" functions directly

```
> K_CO2(15, 30)

[1] 9.089117e-07
attr(,"unit")
[1] "mol/kg-soln"
attr(,"pH scale")
[1] "free"

> K_HCO3(15, 30)

[1] 6.014934e-10
attr(,"unit")
[1] "mol/kg-soln"
attr(,"pH scale")
[1] "free"

> K0_CO2(15, 30)

[1] 0.03852158
attr(,"unit")
[1] "mol/(kg-soln*atm)"

> Ksp_calcite(15, 30, 100)

[1] 3.644549e-07
attr(,"unit")
[1] "(mol/kg-soln)^2"
```

2.1.2 Minimal *aquaenv* definition

```
> ae <- aquaenv(Tc = 15, S = 30)
> ae$K_CO2

[1] 9.089117e-07
attr(,"unit")
[1] "mol/kg-soln"
attr(,"pH scale")
[1] "free"

> ae$Ksp_calcite
```

```
[1] 3.582242e-07
attr(,"unit")
[1] "(mol/kg-soln)^2"

> ae$Ksp_aragonite

[1] 5.643199e-07
attr(,"unit")
[1] "(mol/kg-soln)^2"

> ae <- aquaenv(Tc = 15, S = 30, d = 10)
> ae$K_CO2

[1] 9.09921e-07
attr(,"unit")
[1] "mol/kg-soln"
attr(,"pH scale")
[1] "free"

> ae$Ksp_calcite

[1] 3.588429e-07
attr(,"unit")
[1] "(mol/kg-soln)^2"

> ae$Ksp_aragonite

[1] 5.652276e-07
attr(,"unit")
[1] "(mol/kg-soln)^2"

> names(ae)

 [1] "Tc"           "Tk"           "S"            "Cl"
 [5] "I"            "d"            "hydroP"       "density"
 [9] "SumCO2"       "SumNH4"       "SumH2S"       "SumHNO3"
[13] "SumHNO2"      "SumH3PO4"     "SumSiOH4"     "SumBOH3"
[17] "SumH2SO4"     "SumHF"        "SumBr"        "ClConc"
[21] "Na"           "Mg"           "Ca"           "K"
[25] "Sr"           "molal2molin"  "free2tot"     "free2sws"
[29] "tot2free"     "tot2sws"      "sws2free"     "sws2tot"
[33] "K0_CO2"       "K0_O2"        "CO2_sat"      "O2_sat"
[37] "K_W"          "K_HSO4"       "K_HF"         "K_CO2"
[41] "K_HCO3"       "K_BOH3"       "K_NH4"        "K_H2S"
[45] "K_H3PO4"      "K_H2PO4"      "K_HPO4"       "K_SiOH4"
[49] "K_SiOOH3"     "K_HNO2"       "K_HNO3"       "K_H2SO4"
[53] "K_HS"         "Ksp_calcite"  "Ksp_aragonite"
```

2.1.3 Defining the complete aquaenv system in different ways

```
> Tc <- 15
> S <- 30
> d <- 10
> SumCO2 <- 0.002
> pH <- 8
> TA <- 0.002140323
> pCO2 <- 0.000533576
> CO2 <- 2.055419e-05
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH)
> ae$TA

[1] 0.002140800
attr(,"unit")
[1] "mol/kg-soln"

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA)
> ae$pH

[1] 7.998791
attr(,"pH scale")
[1] "free"

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, CO2 = CO2)
> ae$pH

[1] 7.999293
attr(,"pH scale")
[1] "free"

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pCO2 = pCO2,
+     dsa = TRUE, revelle = TRUE)
> ae$pH

[1] 7.999293
attr(,"pH scale")
[1] "free"

> names(ae)

  [1] "Tc"               "Tk"               "S"
  [4] "Cl"               "I"                "d"
  [7] "hydroP"           "density"          "SumCO2"
 [10] "SumNH4"           "SumH2S"           "SumHNO3"
 [13] "SumHNO2"          "SumH3PO4"         "SumSiOH4"
```

```
 [16] "SumBOH3"          "SumH2SO4"         "SumHF"
 [19] "SumBr"            "ClConc"           "Na"
 [22] "Mg"               "Ca"               "K"
 [25] "Sr"               "molal2molin"      "free2tot"
 [28] "free2sws"         "tot2free"         "tot2sws"
 [31] "sws2free"         "sws2tot"          "KO_CO2"
 [34] "KO_O2"            "CO2_sat"          "O2_sat"
 [37] "K_W"              "K_HSO4"           "K_HF"
 [40] "K_CO2"            "K_HCO3"           "K_BOH3"
 [43] "K_NH4"            "K_H2S"            "K_H3PO4"
 [46] "K_H2PO4"          "K_HPO4"           "K_SiOH4"
 [49] "K_SiOOH3"         "K_HNO2"           "K_HNO3"
 [52] "K_H2SO4"          "K_HS"             "Ksp_calcite"
 [55] "Ksp_aragonite"    "TA"               "pH"
 [58] "pCO2"             "CO2"              "HCO3"
 [61] "CO3"              "BOH3"             "BOH4"
 [64] "OH"               "H3PO4"            "H2PO4"
 [67] "HPO4"             "PO4"              "SiOH4"
 [70] "SiOOH3"           "SiO2OH2"          "H2S"
 [73] "HS"               "S2min"            "NH4"
 [76] "NH3"              "H2SO4"            "HSO4"
 [79] "SO4"              "HF"               "F"
 [82] "HNO3"             "NO3"              "HNO2"
 [85] "NO2"              "omega_calcite"    "omega_aragonite"
 [88] "revelle"          "c1"               "c2"
 [91] "c3"               "dTAdSumCO2"       "b1"
 [94] "b2"               "dTAdSumBOH3"      "so1"
 [97] "so2"              "so3"              "dTAdSumH2SO4"
[100] "f1"               "f2"               "dTAdSumHF"
[103] "dTAdH"            "dTAdKdKdS"        "dTAdKdKdT"
[106] "dTAdKdKdd"        "dTAdKdKdSumH2SO4" "dTAdKdKdSumHF"

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, CO2 = CO2, pCO2 = pCO2)

[1] "Error! Overdetermined system: entered pCO2: 0.000533576 , calculated pCO2: 0.00053357
[1] "Please enter only one of: pH, TA, CO2, or pCO2."

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, TA = TA)

[1] "Error! Overdetermined system: entered TA: 0.002140323 , calculated TA: 0.002140799720
[1] "Please enter only one of: pH, TA, CO2, or pCO2."

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, CO2 = CO2)

[1] "Error! Overdetermined system: entered pH: 8 , calculated pH: 7.99929303203143"
[1] "Please enter only one of: pH, TA, CO2, or pCO2."
```

```
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, pCO2 = pCO2)

[1] "Error! Overdetermined system: entered pH: 8 , calculated pH: 7.99929301525035"
[1] "Please enter only one of: pH, TA, CO2, or pCO2."

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA, CO2 = CO2)

[1] "Error! Overdetermined system: entered TA: 0.002140323 , calculated TA: 0.002140520813
[1] "Please enter only one of: pH, TA, CO2, or pCO2."

> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA, pCO2 = pCO2)

[1] "Error! Overdetermined system: entered TA: 0.002140323 , calculated TA: 0.002140520806
[1] "Please enter only one of: pH, TA, CO2, or pCO2."
```

2.1.4 Cloning the aquaenv system: 1 to 1 and with different pH or TA

```
> Tc <- 15
> S <- 30
> SumCO2 <- 0.002
> TA <- 0.00214
> ae <- aquaenv(Tc, S, SumCO2 = SumCO2, TA = TA)
> aeclone1 <- aquaenv(ae = ae)
> pH <- 9
> aeclone2 <- aquaenv(ae = ae, pH = pH)
> TA <- 0.002
> aeclone3 <- aquaenv(ae = ae, TA = TA)
> ae$pH

[1] 7.99838
attr(,"pH scale")
[1] "free"

> aeclone1$pH

[1] 7.99838
attr(,"pH scale")
[1] "free"

> aeclone2$TA

[1] 0.002982758
attr(,"unit")
[1] "mol/kg-soln"

> aeclone3$pH

[1] 7.548174
attr(,"pH scale")
[1] "free"
```

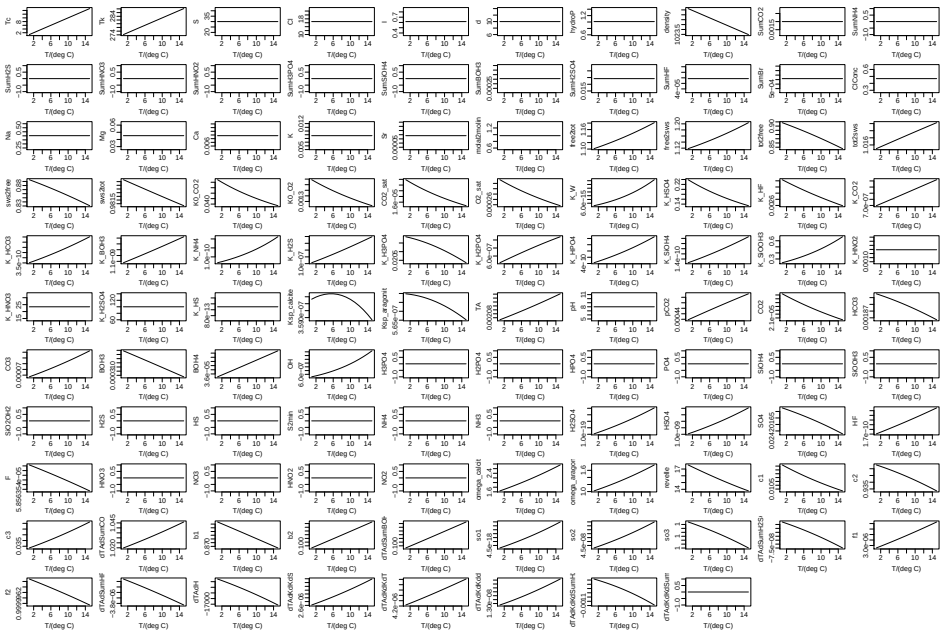
2.1.5 preparing input variables

```
> Tc <- 15
> S <- 10
> pH_NBS <- 8.142777
> SumCO2molar <- 0.002016803
> pH_free <- convert(pH_NBS, "pHscale", "nbs2free", Tc = Tc,
+     S = S)
> SumCO2molin <- convert(SumCO2molar, "conc", "molar2molin",
+     Tc = Tc, S = S)
> ae <- aquaenv(Tc, S, SumCO2 = SumCO2molin, pH = pH_free)
> ae$pH


[1] 8
attr(,"pH scale")
[1] "free"


> ae$SumCO2


[1] 0.002000000
attr(,"unit")
[1] "mol/kg-soln"


> ae$TA


[1] 0.002048921
attr(,"unit")
[1] "mol/kg-soln"
```

2.1.6 Vectors as input variables

(only ONE input variable may be a vector)
(with full output: including the Revelle factor and the DSA properties)

```
> SumCO2 <- 0.002
> pH <- 8
> Tc <- 1:15
> S <- 30
> d <- 10
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, revelle = TRUE,
+     dsa = TRUE)
> plot(ae, xval = Tc, xlab = "T/(deg C)", newdevice = FALSE)
```



extra examples

```
> Tc <- 15
> S <- 1:30
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, revelle = TRUE,
+     dsa = TRUE)
> plot(ae, xval = S, xlab = "S")
> S <- 30
> d <- seq(1, 1000, 100)
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, pH = pH, revelle = TRUE,
+     dsa = TRUE)
> plot(ae, xval = d, xlab = "depth/m")
> TA <- 0.0023
> Tc <- 1:15
> S <- 30
> d <- 10
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA, revelle = TRUE,
+     dsa = TRUE)
> plot(ae, xval = Tc, xlab = "T/(deg C)")
> Tc <- 15
> S <- 1:30
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA, revelle = TRUE,
+     dsa = TRUE)
> plot(ae, xval = S, xlab = "S")
> S <- 30
> d <- seq(1, 1000, 100)
> ae <- aquaenv(Tc, S, d, SumCO2 = SumCO2, TA = TA, revelle = TRUE,
+     dsa = TRUE)
> plot(ae, xval = d, xlab = "depth/m")
```

References

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Hofmann AF, Middelburg J, Soetaert K, Wolf-Gladrow DA, Meysman F (2008b). "pH modelling in aquatic environments: from an alkalinity-based to a proton-based view." *in preparation*.

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