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SolEq: Tools and tutorials for studying solution equilibria

PAPER

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SolEq (Solution Equilibria) is a CD-based package of tutorials designed for teaching equilibria to senior undergraduate students. Between them, they cover the principles and applications of acid-base, redox, solubility, and metal-ligand chemistry in both homogeneous and heterogeneous systems. It also provides the computational software for applying equilibrium principles to real systems (speciation programs, database, ionic strength and van't Hoff corrections *etc*.). The 29 tutorials and 8 computational packages are linked seamlessly *via* tool bar functions. SolEq has been used to support lecture and laboratory courses on environmental chemistry, coordination chemistry and analytical chemistry. It has also been used to create a customised refresher course for a graduate about to embark on a research programme in environmental chemistry.

Introduction

Equilibrium principles play a pivotal role in chemistry. For example, equilibrium processes are critical in the aquatic environment around us, and in the plasma and intracellular fluid within us. We recognise the importance of equilibrium by inclusion of topics such as solubility and acid-base theory in elementary chemistry courses, even though we may not cover them rigorously. However, these principles also underpin more complex systems and applications (*e.g.* environmental, industrial and biological processes, speciation and coordination chemistry).

In spite of the central role that this topic plays in chemistry, we were unable to locate suitable resources to support two undergraduate courses that we are required to teach. One is on 'the energetics of complex formation', an advanced inorganic chemistry course that involves an in-depth treatment of energetic (equilibrium) principles. The other is on aquatic chemistry, with emphasis on equilibrium reactions (metal ion speciation) and redox processes in environmental systems.

Our survey of available resources showed that excellent texts are available in specialist areas. Typically these adopt a chemical energetics (equilibrium) perspective against which to address issues in environmental chemistry[1,2], industrial chemistry[3], and aquatic chemistry[4]. These texts, because of their depth, rigour and specialisation, are not appropriate for courses to non-specialists or for a generic approach. In other areas, such as thermodynamic aspects of coordination chemistry and its applications in biological systems we have found a dearth of suitable teaching resources. We therefore determined to create a resource that would meet our requirements and be suitable for use by middle and advanced-level university undergraduates and by graduate students whose research involves any aspect of solution equilibria.

Such a resource would support a generic approach to solution equilibrium by drawing together redox, acid-base, metal-ligand and solubility equilibrium in one integrated package. It would also provide adequate, self-contained teaching resources in all of these areas, especially for metal-ligand systems. It was our premise that effective teaching of solution equilibrium should involve not only the conceptual and theoretical aspects of equilibrium, but also its application in a wide range of real systems. For this reason we wanted students to move seamlessly from theory to problem solving. This is not easy to achieve using a conventional text-book approach, since many of the problems relevant to equilibrium systems (*e.g.* speciation, buffer, and polyprotic acid calculations) involve complex calculations for which computational software is necessary. However, a CD could include the computational software necessary to effect calculations so that a single resource based on a CD would facilitate the integration of theory and problem solving. A CD would also allow us to include material which cannot be incorporated into text (*e.g.* titration simulations) and all the material would be readily accessible to tutors who wished to use it to enrich lectures and other classroom teaching. We also believe that this contemporary technology provides greater focus for the less well motivated student, and encourages exploration beyond the limits of any prescribed course.

For all these reasons it seemed appropriate to develop a CD rather than a text-book. In this paper we describe the resource, SolEq, which we developed to meet these needs. We report how the SolEq tutorials provide new generic resources for the teaching of solution equilibrium, how they use computational tools to quantitatively apply equilibrium principles to real systems, and how they have been applied in a number of teaching situations.

An overview of SolEq.

The SolEq package is available on CD and is Windows 95/98/NT compatible. It contains 29 tutorials which are listed in Table 1. They are designed to allow students to:

- work through the principles of solution equilibrium;
- facilitate application of equilibrium concepts to problems in multi-component real systems;
- effect relevant calculations and teach computational skills through use of provided software;
- develop student familiarity with equilibrium databases and speciation programs, with ionic strength corrections and use of the van't Hoff equation;
- provide explanation of background theory to the computational software in specific tutorials or Help files.

Some tutorials introduce the simulation packages and software. For example, tutorial 29 'Metal/Ligand Titration Simulations' instructs in the use of the program Metal/Ligand Titrations. This program can simulate the effect of the magnitude of log $K_1(M + L = ML)$ on the metal-ligand titration curve (specifically the effect of M^{z+} on the L/H_nL^{n+} buffer region, $M^{z+} + H_nL^{n+} = ML^{z+} + nH^+$). The shift in pH range for the buffer region and the change in metal or ligand speciation can be demonstrated simultaneously as the pK_a value(s) of H_nL^{n+} and/or log K_1 are varied.

The text incorporates many hypertext-active links; double-clicking on one of these activates a window with a linked file that contains additional information (*e.g.* derivation of equations) or illustrations. For example, tutorial 18 'Acid Rain' includes striking pictorial images of pristine and damaged environmental systems and graphs of acid or NO_x deposition in Europe. Some tutorials include simulations which allow the display of real-time changes in pH titration curves, buffer capacity plots, distribution curve plots *etc.* through varying the number and magnitude of pK_a values, the metal/ligand ratio, the ionic strength, or reagent concentrations.

As table 1 shows, there is an introductory tutorial and the remainder are divided into four main groups: Homogeneous Systems (Principles; Applications), and Heterogeneous Systems (Principles; Applications). Each tutorial is also graded according to difficulty: Level 1 tutorials are appropriate for years 1 and 2, Level 2 for year 3 (and the more capable year 2 students), Level 3 for years 3 and 4. Some of the topics (*e.g.* principles of metal-ligand equilibria in tutorials 10, 12 and 13) are covered in considerably more detail than in available textbooks. Each tutorial is structured as a series of tabbed 'book' pages; i.e. they have a 'softbook' format. Most pages have exercises and worked answers. Each tutorial commences with a list of Learning Objectives, and finishes with a Summary and List of References, and can be completed in 1 to 5 hours.

The tutorials are supported by two titration simulations and eight software packages (*e.g.* for speciation calculations). These can be used as stand-alone items (*e.g.* in conjunction with the teacher's own exercises) or accessed from the tutorial pages *via* tool bar icons.

Voice files that provide an introductory overview to the package in English, Swedish, Russian, German, French, and Japanese are incorporated into the package.

Student feedback on the use of SolEq has been obtained by exit questionnaires after laboratory applications, and from informal discussions with and observation of students using the package.

Examples of Use

Over a three year period, different parts of the package have been used by university chemistry students in several countries. The flexibility of the package is illustrated by the following examples of its use.

Computer-generated lecture demonstrations

Material from some tutorials has been selected and used to enrich lectures with visual displays and demonstrations. For example, one of the objectives of a lecture course on 'Inorganic Energetics' is that students should learn to use a database of stability constants (*viz.* ML-Database) and to carry out speciation calculations (using Species). We have used exercises from Tutorial 13 'Macrocyclics' and Tutorial 15 'Selectivity' to help students to learn these skills. Other examples of the incorporation of SolEq material into lectures include

- incorporation of pH titration and buffer capacity plots into lectures on polyprotic acids and buffers
- use of simulation packages to introduce complex topics and generate an initial overall appreciation of the concepts involved.

In all these examples we have introduced the relevant software at the appropriate time in a lecture to demonstrate key principles. In our experience this has been an effective way of encouraging the students to use the software in their own time (using Help files or a dedicated tutorial) and in this way improve their skills.

A lecture course on complex formation

For three years a course on complex formation for third year students at the University of Canterbury has been taught using, as the sole reference work, the four tutorials 'Thermodynamics' (number 10), 'Chelates' (number 12), 'Macrocyclics' (number 13) and 'Selectivity' (number 15). The course is nominally nine lectures long, but the directed use of the SolEq package has allowed us to adopt a more student-centred approach in which the students take more responsibility for their learning. The relevant tutorials and software packages in SolEq are demonstrated to the students by use of computer projection facilities in the first and second lectures. The remaining seven lecture slots are used to focus their personal study for which students have unlimited access to SolEq on computers in the departmental computer room, and in the students' coffee room and in the library. The approach is rooted in the identification and exploration of the factors that control the formation of stable complexes.

Table 1: SolEq modules

Tutorials

Introduction

1. An introduction to solution equilibria (lg K, ΔG, ΔH and ΔS)

Principles –homogeneous:

Level 1*

2. Acids and bases (protonation, acid dissociation, base hydrolysis)
3. Buffers (properties, preparation and buffer capacity)
4. Introduction to metal-complex formation (basic principles)
5. Complex formation (mono- and poly-dentate ligands)
6. Stability constants (stepwise (K_n) and cumulative constants (β_n); use of $\beta_{p,q,r}$)

Level 2:

7. Polyprotic acids.
8. Redox equilibria (balancing equations, E, pε, Nernst equation)
9. Potentiometric titrations (redox titrations, *e.g.* Ce^{4+}/Fe^{2+})
10. Thermodynamics (ΔG, ΔH and ΔS; temperature and ionic strength effects)
11. Speciation (a primer on setting up calculations and interpreting curves)
12. Chelates (chelate effect; denticity; ring size; applications)
13. Macrocyclics (macrocylic effect; N and O, as well as N,O donors; cryptates and calixarenes)

Level 3

14. Electron activity (concepts; pε-pH, pε-log C; calculations)
15. Selectivity (thermodynamic basis of hard/soft, class A/B classifications)

Applications –homogeneous:

Level 2

16. Metal speciation in natural waters (modelling of Cu^{2+}, Zn^{2+} and Pb^{2+})
17. Metal speciation in seawater (iterative calculation methods)
18. Acid rain (quantitative analysis of acidity-generating equilibria)
19. Trace metals in blood plasma (low molecular mass ligands and proteins)
20. Chelation therapy (use of chelates to remove toxic metals)

Level 3:

21. Marine carbon dioxide system (solubility of CO_2, effect of pH)

Principles –heterogeneous:

Level 2:

22. Solubility and solubility products (molecular and ionic solutes)
23. Complexation and solubility (effect of complexation and pH on solubility)
24. Precipitation titrations (volumetric analysis)

Applications – heterogeneous:

Level 2:

25. Mineral solubility in complexing media (simulating soil weathering)
26. Treatment of metal-contaminated soil (chelates, electrokinetics)
27. Lake equilibria; Lake Baringo, Kenya (speciation of major and trace metals)

Titration simulations:

Level 2:

28. Acid/base titration simulations (with simultaneous speciation)
29. Metal/ligand titration simulations (with simultaneous speciation)

Software Packages:

ML-Database, a database of stability constants for 18,000 metal-ligand pairs, a selected subset from the IUPAC Stability Constants Database.
Buffers, for exploring buffer properties, buffer capacity and for calculations.
Species, for speciation calculations in multi-component, multi-phase systems.
Titration City, to simulate curves for acid-base, redox, and precipitation titrations.
Acid/Base Titrations, to create and display titration and speciation curves in real time.
Metal/Ligand Titrations, to create titration and speciation curves from stability constants.
KvI, to calculate the effect of ionic strength on K (Davies equation).
KvT, to calculate the effect of temperature on K (van't Hoff equation).

* In the context of a three-year B.Sc., Level 1 tutorials are appropriate for years 1 and 2, Level 2 for year 3 (and the more capable year 2 students), Level 3 for years 3 and 4.

The course content is best illustrated by some of the questions that students are required to explore using the SolEq package:

- Is Cd^{2+} a Class A (Hard) or Class B (Soft) metal ion? Students discover the answer by calculating the speciation of Cd^{2+} as a function of pH in a solution containing Cd^{2+}, dithizone (diphenylthiocarbazone) and acetylacetone (2, 4 pentandione) at millimolar concentrations.
- Under what conditions can a negative chelate effect occur? (Students calculate the effect of total concentration on the speciation of Zn^{2+} in a Zn^{2+}-ethylenediamine-triethylenetetramine mixture).
- Establish that when Gd(DOTA) is used as a MRI reagent at the therapeutic dose, DOTA is not sequestered by plasma Ca.
- Establish that 1 mM cyclam is able to complex 1 mM Cu^{2+} quantitatively, even in a 1000-fold excess of triethylenetetramine.
- In an EDTA titration of Ca^{2+} in the presence of Zn^{2+} at pH 10.0, what is the minimum concentration of CN^- required to mask 1 mM Zn^{2+} in the presence of 1 mM Ca^{2+} and 1 mM EDTA?

The SolEq package makes this approach possible because it allows the students to move seamlessly between text, exercises, and supporting software such as 'Species' (for calculations) and 'ML-Database' (for information retrieval). For all exercises, the student has access to worked answers through hypertext links.

Laboratory application I: Speciation calculations

Tutorial 16 'Metal speciation in natural waters' has been used for 3 years with a third year Environmental/Analytical laboratory course at the University of Canterbury. This tutorial introduces the database of stability constants (ML-Database) and takes the student through methods for correcting stability constants for ionic strength effects (KvI software). Through links with the software package Species, students complete calculations on the speciation of Cu^{2+}, Zn^{2+} and Pb^{2+} and are thus shown that the speciation of each metal ion is distinctive and that its speciation in humic, fresh and sea waters is very different.

With this background, students are expected to be ready to work on their own problems. Alternatively they can choose, or the instructor can assign, one of the in-built projects. As an example, one of these is a project concerning the discharge of an aluminium-rich waste solution from a water treatment plant into a river; it illustrates the complexity of the problems that can be attempted.

'A factory discharge into a river contains 10^{-3} M Al^{3+}. The discharge is diluted 50-fold on merging with the river. The major ion composition in the river is $[Ca^{2+}]_T$ = 0.0006 M, $[Mg^{2+}]_T$ = 0.00007 M, $[F^-]_T$ = 0.00005 M and $[SO_4^{2-}]_T$ = 0.0001 M. The river also contains 15 ppm fulvic acid, which may be modelled as 7.5 x 10^{-6} M malonic acid. The river pH is 4.9.

Al(malonate) complexes, Al-F complexes and the $AlSO_4^+$ complex are not toxic to fish, whereas the free Al^{3+} ion is. Determine whether the concentration of toxic Al exceeds the threshold of 5 x 10^{-6} M for survival of fish. Would the same conclusion be made if the river contained less fulvic acid (say 1.5 ppm)?

Use Mini-SCDatabase to obtain the stability constants for relevant Al complexes and use KvI to adjust them to the required ionic strength. Use the provided file MineAl.spc as a template to establish your Species input file'.

This and other problems have sometimes been set for students who have not previously used SolEq. In these cases, a 10 minute introduction from the instructor has been enough to enable the students to get started. The instructor also needs to interact with the students when they are ready to start the Species calculations and again when they start their project assignment. This tutorial plus assignment takes approximately 3.5 hours. Students (working individually or in pairs) frequently remain at the terminal for this length of time, without apparent loss of concentration. In conversation with them, it appears that they are enthused by the fact that after a comparatively short practical experience (plus background course work) they have access to, understanding of, and adequate competence with, software and databases that can facilitate answers to complex environmental questions.

Feedback from exit questionnaires has been uniformly positive.

Laboratory application II: A Food Technology course

The SolEq package has been used at the Moscow State University of Food Technology to support the laboratory course in Physical and Colloid Chemistry. These students are training to be Food Technologists in the bakery, beer, wine, sugar beet and plant oil based industries and do not have strong chemical backgrounds. For this reason the students are provided with a 14-page manual in Russian (written in-house) which includes instructions on how to use the selected software packages Acid/Base Titrations, Species and ML-Database.

The manual includes 10 exercises with questions focused on particular food-industry cases. For example, students use Acid/Base Titrations to calculate and print out the speciation curve for citric acid and so determine the optimal pH for crystallization of citric acid and crystallization of tripotassium citrate. Students follow up the experimental (conductivity) determination of pK_a for acetic acid by calculating the speciation curves. This demonstrates that acetic acid (pK_a = 4.8) exists only as CH_3COOH at pH < 3 and only as CH_3COO^- at pH > 7, whereas at 3 < pH < 7 there is a mixture of both species!

Other questions which students investigate are

- the pH range over which glycine exists in the isoelectric state;
- whether Ca^{2+} will form complexes with glycine in blood plasma (at pH 7);
- the pH at which the Fe^{3+}-H^+ and Al^{3+}-H^+ systems best initiate coagulation of sols.

A refresher course and research tool

The SolEq programs have been used as a research tool at Queen's University, Belfast by a graduate commencing measurements on stability constants for ternary systems relevant to natural waters. This student was able to use selected tutorials (*e.g.*16 'Metal speciation in natural waters' and 29 'Metal/ligand titration simulations'), the extensive Help files (*e.g.* the definitions and standard reporting protocols for stability constants), together with the software package Species, to answer questions like

- what concentrations of metal and ligand will be needed to generate adequate end points?
- how many inflexions will the titration curve have?

The Species software allows distribution diagrams to be generated from the determined stability constants after following the appropriate tutorial (number 11, 'Speciation'). Since SolEq contains files for modelling trace metal complexation in various types of natural waters the ternary complexation data could be incorporated into these files thus making it possible to answer questions such as "Could ternary complexes contribute significantly to the speciation expected under typical natural water conditions?"

In this way the student designed her own refresher course through which she became proficient with the calculation and simulation programs, and used the SolEq package to aid experimental design.

Discussion

The examples of applications of SolEq illustrate that we have met our objective of creating a flexible resource. Student feedback has been largely formative and has led to improvements in the presentation and wording, to clarification of the learning objectives, and to an increase in the number of exercises embedded in the tutorials. Student feedback also led to the incorporation of the facility for students to download a hard copy of each Principles tutorial for personal records or study (this is non-interactive, but it has been so constructed to contain all text including hypertext-linked files, problems and worked answers to exercises).

Student responses on feedback questionnaires indicate that the package is technically satisfactory: analysis of the responses shows that most students find

- the instructions are adequate;
- the tool bar functions and hypertext links are easy to operate and are valuable;
- the pictorial and graphical representations are well conceived and informative;
- the tutorials are of appropriate length and challenge;
- the learning environment is to their liking.

Students whose first language is not English have commented favourably on the use of the voice files giving an introductory overview.

We have observed a high level of commitment from students to the set assignments and we have noted that students make frequent use of the tutorials in their own time. We conclude from these observations that the package is motivating. We suggest that one reason for this is that SolEq provides bridges between the teaching of theory and its application to problems in real systems. We believe that this is a benefit of an integrated text/computational system that cannot be provided as comprehensively or in such a focussed manner by a textbook.

Our experience with the SolEq package has convinced us of the value of a CD that has allowed us to combine in a single resource the key qualities of a textbook with the interactive computational and graphing facilities of software.

Availability

Demonstration tutorials and the programme Species can be downloaded from the SolEq web site at www.acadsoft.co.uk. The demonstration tutorials cover each level, with examples from both Principles and Applications modules. The web site also features an enquiry form for additional information and a downloadable or email order form.

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