Henry's Law Constant Program

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This is a review of Syracuse Research Corporation's Henry's Law Constant Program (version 2).[1] The program estimates Henry's law constants using both bond and group additive methods originally developed by Sydney Benson[2] and applied to Henry's law constants by Hine and Mookerjee.[3] This program uses an expanded set of bond and group constants that have been refined by Meylan and Howard,[4] the authors of the program.

Program installation was simple, and only a couple of minutes were required to create a subdirectory on the hard disk, copy the program files to this subdirectory, and run the program by typing HENRY at the DOS prompt. Minimal requirements for using the program are an IBM compatible computer with 270 KB of free memory. The program was tested on a 486 66 MHz IBM compatible computer from Greenleaf International, Inc. with 8 MB of RAM and SVGA monitor, and it worked fine in all aspects. Organization of the screen output was simple and intuitive.

While the program can be used by a novice without reference to the manual, the manuals were short, well written, to the point, and easy to use. In particular they pointed out how to use the program to correctly estimate Henry's law constants and where to be careful to avoid misusing the results. The dataset and an accompanying paper[5] that were supplied with the program clearly discuss the reliability of the experimental data, including the references to the original literature, on which the method is based. The units on the Henry's law constant referred to in the *Units Conversion of Henry's Results* section of the manual would be better described as mol of solute per unit volume of air divided by mol of solute per unit volume of water, instead of unitless.

The Henry's law constants generated by the program were compared with experimental Henry's law constants for 1-nonanol, 2-decanone, 1,2-dimethylbenzene, pentachlorobenzene, 4-bromochlorobenzene, benzo[*a*]pyrene, 2-chlorobiphenyl, and *n*-propanethiol.[6] None of these compounds are in the data bases used to either generate or validate the bond and group additive methods used in this program. Experimental Henry's law constants for these compounds varied over ca. four orders of magnitude from 5.1×10^{-3}–1.2×10^{-6} atm m^3/mol. The standard errors of the log of the ratio of the molar concentrations in the gas and aqueous phases were 0.14 and 0.15 for both the bond and group methods, respectively, which compares well with the standard errors of 0.12 and 0.45 obtained by Hine and Mookerjee.[3] Correlation coefficients of 0.94 and 0.97 were obtained from linear regressions for the bond and group estimates, respectively, versus the experimental log of the ratio of the molar concentrations in the gas and aqueous phases. Again the correlation coefficient for the bond method compares favorably with the correlation coefficient of 0.96 obtained by the authors[4] for 76 compounds used to validate the method.

Structural input to the program uses SMILES notation.[7] Only about an hour's time with the tutorial, *A Brief Description of SMILES Notation*, was required to bring me to a point where I could easily write SMILES notation for moderately complicated structures like the polycyclic aromatic hydrocarbon, pyrene. A separate ~20 000 compound database, the CAS Number Database,[8] provides an alternate method of input to the program. Entering the CAS registry number, 50-32-8, for benzo[*a*]pyrene quickly retrieved the Smiles notation, c(c(c(cc1)ccc2)c2cc3)(c3cc(c4ccc5)c5)c14, for this compound, from the CAS Number Database. Since these CAS registry numbers were obtained from a U.S. EPA file, the compounds in the database are likely to be of environmental interest. The CAS Number Database is ~2.3 MB and, since it must reside in the same subdirectory as the file HENRY.EXE, requires the use of a hard disk.

The program has a number of convenient features. For example, function keys allow the user to easily clear the current input or recall the previous input. Much of the USER's Guide and SMILES Notation manuals are available as on screen help. In each session the results of all estimates of Henry's law constants are automatically appended to the file HLC*.DAT, where * is a sequential number from 1 to 19 that is incremented in each new session. Up to 100 results can also be saved to a User Input File. Both saving and recalling results saved to this User Input file are quickly accomplished via function keys accessible from the input screen. The results of calculation can also be saved to a file specified by the user at program initiation. These handy features allow the user to easily retrieve the results without rerunning the program.

When the program output was directed to a user specified file, by starting the program with the command HENRY> NAME.DAT, or to a printer, by starting the program with the command, HENRY> PRN, no output was sent to the screen. I found this situation mildly annoying. Printing the results, while simultaneously viewing the results on screen can, however, be accomplished by using Print Scrn from within the program or by sending a Ctrl Print Scrn command to the printer prior to starting the program.

A version of the program that runs under MicroSoft Windows was also supplied. During the Windows installation, the error message, *cannot find the file HENRYWHELP.HLP*, appeared. A check of the files on the floppy disk supplied with the program revealed that this file is actually called HENWHELP.HLP. After copying this file to the name HENRYWHELP.HLP, the Windows installation was completed without any problems. When help was accessed from the menu, the message, *cannot open Help file* appeared, but clicking OK and then opening the file HENRYWHELP.HLP from the Help window activated the help file and help worked from this point on. These two minor problems are probably related and likely easily fixed

by renaming some program files. Perhaps because I am not a die-hard Windows user, I found the DOS version of the program easier and quicker to use than the Windows version.

A weakness of the bond and group additive methods is that they can give poor results when applied to large structures or compounds containing many polar functional groups. Version 2 of the Henry's Law Constant Program addresses this limitation by providing a modified approach to the bond contribution method that starts with a structure similar to the desired structure, for which the Henry's law constant is known, and then swaps bond contributions to yield Henry's law constant estimates for the desired structure. The program manual uses 2-isobutyl-3-methoxypyrazine to illustrate this approach and produces a result of 2.59×10^{-5} atm m^3/mol that is in reasonable agreement with the measured value of 5.24×10^{-5} atm m^3/mol.[9] I attempted to use this method to estimate the Henry's law constant for pentachlorophenol, starting with a Henry's law constant for pentachlorobenzene of 1.20×10^{-3} atm m^3/mol that was first estimated using the unmodified approach. The unmodified estimate of the Henry's law constant for pentachlorophenol of 1.25×10^{-7} atm m^3/mol is nearly an order of magnitude different than the experimental value of 2.4×10^{-8} atm m^3/mol. Unfortunately the modified method did not improve on this estimate but instead yielded a value of 1.25×10^{-7} atm m^3/mol that was the same as that generated by the unmodified method. Attempts to show that the modified method improved the estimates of Henry's law constants for pentachlorobenzene, starting with 1,2,3,4-tetrachlorobenzene, and benzo[*a*]pyrene, starting with pyrene, also yielded the same values as the unmodified method.

In summary I found this program easy to use and reliable and can highly recommend it to anyone who routinely uses Henry's law constants in calculating how chemical species partition at equilibrium at 25 °C across an air/water interface.

REFERENCES AND NOTES

(1) Syracuse Research Corporation, Merrill Lane Syracuse, New York 13210-4080 (315-426-3200, FAX 315-426-3429). The program, which comes in both DOS and MicroSoft Windows formats, costs $400.
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(8) *CAS Number Database*; Syracuse Research Corporation; Merrill Lane Syracuse, New York, 13210-4080. This database is sold separately and costs $100.
(9) Buttery, R. G. et al. *J. Agric. Food Chem.* **1971**, *19*, 1045−8.

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