

This Week's Citation Classic®

Izatt R M, Bradshaw J S, Nielsen S A, Lamb J D, Christensen J J & Sen D.

Thermodynamic and kinetic data for cation-macrocycle interaction.
Chem. Rev. 85:271-339, 1985.

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Thermodynamic and kinetic data for cation-macrocycle interaction are compiled and discussed. Correlations are shown between log *K* values and various cation and macrocycle parameters. [The SC[®] indicates that this paper has been cited in more than 445 publications.]

suggesting that macrocycles with selective cation complexation properties could be prepared.

The frequent citation of this review article can be attributed to three factors. First, the compiled data are useful to workers who are interested in the design of new macrocycles for the above and other purposes. Second, the availability of a large literature base on macrocyclic compounds has enabled workers to see the promise that these molecules have in the investigation of interesting chemical problems. Third, macrocyclic chemistry is perceived by an increasing number of scientists as providing a means to design novel molecules with built-in selectivity properties, and the availability of thermodynamic data is important in this design process.

The number of workers in macrocyclic chemistry has increased rapidly during the past 25 years. The 1987 Nobel Prize in chemistry was awarded to three of the early workers, Donald J. Cram, Jean-Marie Lehn, and Pedersen. Continued interest in the subject is reflected in a follow-up *Chemical Reviews* article in 1991 on the same subject plus anion complexation.⁴ In this follow-up article, the number of references has increased threefold over that in the 1985 review that covered data prior to 1984. The number of pages in the 1991 article is 364 compared to 68 in the 1985 review. In 1992, a separate *Chemical Reviews* article on macrocycle-neutral molecule interaction was published.⁵

The existence of a highly cited review article on thermodynamic and kinetic data in a rapidly expanding field suggests that such data are valuable to workers in that field. It would be worthwhile for funding agencies to consider this as they determine those areas that should be supported. We appreciate the continuing support we have received for our thermodynamic work from the National Science Foundation, the Department of Energy—Office of Basic Energy Sciences, and the Office of Naval Research.

Thermodynamic and Kinetic Data Can Be Useful

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The publication in 1967¹ of Charles J. Pedersen's synthesis and characterization of over 30 new cyclic polyether macrocycles initiated tremendous and continuing interest in the scientific community. This interest was stimulated by the possibilities macrocycles offered to the creative chemist to investigate molecular recognition in new ways. How molecules and ions recognize other molecules and ions has long intrigued chemists. Over the past 25 years, macrocycle hosts have been prepared that elucidated much new chemistry involving a variety of guest species of inorganic, organic, and biochemical interest. Molecular recognition principles have led also to new and improved selective separation reagents. The development of this new field of macrocyclic chemistry has been aided greatly by the availability of a large number of *K*, *AH*, and *AS* values for host-guest interaction. Quantitative thermodynamic data provide a basis for the design of new molecules with predetermined properties such as superior guest binding strengths, guest selectivities, and superior catalytic properties. Early work by us^{2,3} showed a correlation between log *K* for cation-macrocycle interaction and cation diameter

1. Pedersen C J. Cyclic polyethers and their complexes with metal salts. *J. Amer. Chem. Soc.* 89:7017-36, 1967. (Cited 1,900 times.)

[See also: Pedersen C J. Citation Classic. *Current Contents/Engineering, Technology & Applied Sciences* 16(32): 18, 12 August 1985, and *Current Contents/Physical, Chemical & Earth Sciences* 25(32):18, 12 August 1985.]

2. Izatt R M, Rytting J H, Nelson D P, Haymore B L & Christensen J J. Binding of alkali metal ions by cyclic polyethers: significance in ion transport processes. *Science* 164:443-4, 1969.

3. Izatt R M, Nelson D P, Rytting J H, Haymore B L, St Christensen J J. A calorimetric study of the interaction in aqueous solution of several uni- and bivalent metal ions with the cyclic polyether dicyclohexyl-18-crown-6 at 10, 25, and 40 °C. *J. Amer. Chem. Soc.* 93:1619-23, 1971. (Cited 170 times)

4. Izatt R M, Pawlak K, Bradshaw J S & Bruening R L. Thermodynamic and kinetic data for macrocycle interactions with cations and anions. *Chem. Rev.* 91:1721-2085, 1991.

5. Izatt R M, Bradshaw J S, Pawlak K, Biening R L & Tarbet B J. Thermodynamic and kinetic data for macrocycle interaction with neutral molecules. *Chem. Rev.* 92:1261-354, 1992.

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