

Kosower E. M. The effect of solvent on spectra. I. A new empirical measure of solvent polarity: Z-values. *J. Amer. Chem. Soc.* **80**:325360, 1958.
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The discovery that the charge-transfer absorption band of 1-alkyl-4-carbomethoxy pyridinium iodides was enormously sensitive to the nature of the solvent in which it was measured led to the proposal that the transition energies corresponding to the band maxima, expressed in kcal/mol, be utilized as empirical measures of solvent polarity, called Z-values. The convenience and speed with which Z-values may be obtained, through measurement of a spectroscopic maximum in the solvent of interest, accounts for their widespread use. [The *SCI*[®] indicates that this paper has been cited over 630 times since 1961.]

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"The Zvalue papers presented a method for measuring the polarity of solvents which was simple, fast, and understandable in a precise way on the molecular level. Grunwald and Winstein had recognized the limitations of the dielectric constant in 1948 and had introduced an empirical parameter of solvent polarity (Y-value) based on the rate of reaction of tbutyl chloride.¹ I was very much aware of the usefulness of Yvalues since I had done my PhD thesis under Winstein's direction.

"The discovery of the phenomenon which led to the creation of Z-values was the result of good luck. As a National Institutes of Health postdoctoral fellow with Frank Westheimer at Harvard in 1954, I needed to examine the reaction of hydroxide ion with 1-methylpyridinium ion. The only 1methylpyridinium salt which was convenient to prepare was the iodide. Spectra of the salt revealed a new species, a charge transfer complex of 1methylpyridinium ion (the

acceptor) and iodide (the donor).² Our work was done shortly after Mulliken's brilliant papers on charge transfer complexation in 1952,² so that the theoretical explanation was readily available.

"At the University of Wisconsin in 1956, in order to make the charge transfer transition easier to observe, I added a 4-carbomethoxy group to the pyridinium ring and changed the 1methyl group to a 1ethyl group to increase solubility. The position of the light absorption of 1-ethyl-4-carbomethoxy pyridinium iodide was then very sensitive to the nature of the solvent!

"It was logical to see if solvent dependence were of the same kind represented by the Yvalues mentioned above. I chose solvent mixtures at random and, plotting the data as I obtained them, was disheartened to see a great scatter. However, I persisted and was rewarded with three straight lines, one for each solvent mixture (ethanolwater, methanolwater, and acetonewater). Furthermore, the lines extrapolated to the Y-value for pure water! Thus, it was clear that the position of the charge transfer bands reflected the polarity of the solvent.

"I converted the positions of the bands into energies (kcal/mole) to make it convenient for a chemist to use. I resisted the suggestion that I call the numbers Kvalues, and chose Z-values because they came after Yvalues. The usefulness of Z-values was extended by Dimroth and Reichardt in 1963 with $E_r(30)$ values, based on a pyridinium salt which is more soluble in organic solvents.³ The theoretical explanation for the high solvent sensitivity of the charge transfer bands, presented in the paper cited, still appears to be valid with some modifications.

"We and others have found the Z-values (and $E_r(30)$ values) to be very useful for correlating spectroscopic and kinetic data. Most recently, Dodiuk, Kanety, and myself at the Tel-Aviv University have found that solvent molecule motion controls the rate of an intramolecular electron transfer reaction by correlating excited state kinetic constants with a solvent polarity parameter.⁴

"We all know that there are sometimes difficulties in having articles published. In contrast, the Z-value papers were quickly accepted and were well-received, an exception to the rule."

1. Grunwald E & Winstein S. The correlation of solvolysis rates. *J. Amer. Chem. Soc.* **70**:846-954, 1948.

2. Mulliken R S. Molecular compounds and their spectra II. *J. Amer. Chem. Soc.* **74**:811-24, 1952.

3. Dimroth K, Reichardt C, Siepmann T & Bohlmann F. Über PyridiniumNphenol betaine und ihre Verwendung zur Charakterisierung der Polarität von Lösungsmitteln. *J. Liebig's Annalen Chemie* **661**:137, 1963.

4. Kosower E M, Dodiuk H & Kanety H. Intramolecular donor-acceptor systems. IV. Solvent effects on radiative and nonradiative processes for the charge transfer states of N-arylamino naphthalenesulfonates. *J. Amer. Chem. Soc.* **100**:417-989, 1978.