

Solvatochromism and Solvent Polarity Scales

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Received September 5, 1989 (Revised Manuscript Received March 20, 1990)

Merocyanines: Applications in New Materials and in Solvatochromism

Merocyanine dyes are gaining predominance due to their diverse applications in various fields. In neurophysiology, voltage-sensitive merocyanine dyes have been found to be of great potential for monitoring neuronal activity for a single neuron as well as a large neuronal network. Of the several hundred compounds studied so far, merocyanine dyes exhibit the highest voltage sensitivity.² Electrochromic merocyanine dyes are reported to be suitable calibration probes for monitoring membrane potentials since electrochromism provides a fast and completely characterized uniform response to membrane potentials.³

Because of the charge asymmetry in these molecules, merocyanine dyes exhibit the largest known molecular hyperpolarizability in nonlinear optics. Applications of this phenomenon comprise information processing, integrated optics, laser doublers, and liquid crystals.⁴

In photochromism, merocyanines, especially the spiro pyrans, have been widely cited as photochromic dyes in the past three decades.⁵ The photoisomerization of spiro benzopyran derivatives, as well as azobenzenes and other photochromic compounds, as components in polymer films, is exploited for its potential applicability in generating erasable photomemory systems.⁶ A new class of merocyanine dyes, the so-called photodynamic macromolecules, are expected to be capable of formation of inclusion complexes, analogous to hosts such as cyclodextrins and other synthetic macromolecules.⁷

In the present search for new materials for technological applications, certain merocyanine dyes have been used as color sensors and heat-developable light sensors. The changing specific resistance of a particular merocyanine dye as a film on illumination has led to an intermediate state between an insulator and a semiconductor. These features lead to special photoelectrochemical properties.⁸ Merocyanines have also been reported to be used in color electrophotographic processes, optical recording materials, and IR-passive shutters for near-IR lasers, as well as photovoltaic devices and photosensitizers.⁹

Erwin Buncel is Professor of Chemistry at Queen's University. (For a bibliography summarizing his earlier research activities, see: *Acc. Chem. Res.* 1979, 12, 42.) Since 1980 the research of Buncel's group has ranged over several areas—reactions of electron-deficient aromatics with bases, catalysis in strongly acidic and basic media, carbanion mechanisms, isotope effects on reaction rates and equilibria, and most recently, metal ion catalysis in nucleophilic displacements at carbon, phosphorus, and sulfur centers—always applying the principles of physical organic chemistry. In 1985, Buncel was the recipient of the Syntex Award in Physical Organic Chemistry from the Chemical Institute of Canada.

Srinivasan Rajagopal obtained his B.Sc. and M.Sc. degrees from Vivekananda College, Madras, India, and his Ph.D. degree from Queen's University, Canada, in 1987, where he worked on azo and azoxy dyes. Presently he is a Research Associate in the Radiochemistry unit of the Montreal Neurological Institute. His current interests are in the synthesis and pharmacokinetics of experimental positron-emitting radiopharmaceuticals for brain imaging studies using positron emission tomography (PET), and autoradiography.

In solvatochromism, merocyanines exhibit the largest known bathochromic shift with change in solvent polarity. It is this property that is of chief concern to us in the present Account.

The phenomenon of solvatochromism arises when a solute dissolved in solvents of varying polarity manifests a pronounced change in position, intensity, and shape of an absorption band. A bathochromic (red) shift and a hypsochromic (blue) shift with increasing solvent polarity are called positive and negative solvatochromism, respectively. A change from bathochromic to hypsochromic, or vice versa, with increase in solvent polarity, is called *reverse* solvatochromism. The pronounced change in the position of the absorption band has been used as a probe to determine one of the properties of the solvent, namely, its *polarity*. However, the term solvent polarity is yet to be defined precisely although several attempts have been made so far. The important point concerning the so-called polarity of a solvent is *its overall solvation capability*, which is the cumulative effect of all the solvent-solute interactions, excluding those such as protonation, oxidation, reduction, complexation, etc., which might lead to a chemical change of the solute.¹⁰

Solvatochromic compounds are those solutes that induce a change in the color of the solution with a change in solvent polarity. Typically, solvatochromic compounds can be described by two extreme resonance contributing structures: one form is quinoidal, nonpolarized, and formally nonaromatic; the other is zwitterionic, polarized, and fully aromatic. The change in the absorption band with solvent arises from variation in the contribution of these canonical forms to the overall resonance hybrid.¹¹

Recently we chose a family of diazomethine merocyanines, or azo merocyanines for short, 1-6, which include two novel compounds, 2 and 4, for the purpose of examining their chromogenic properties and in particular their solvatochromism. Compounds of this type arose when we extended studies of the acid-catalyzed

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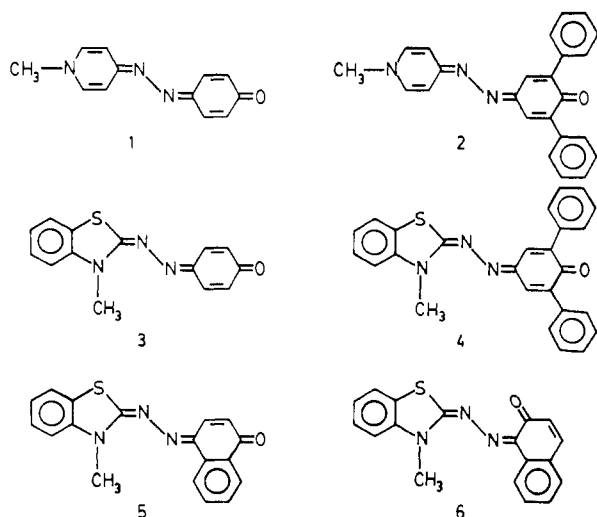
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Wallach rearrangement¹² from the originally studied azoxyarenes into the phenyl azoxy pyridine series.^{13a-d,f}

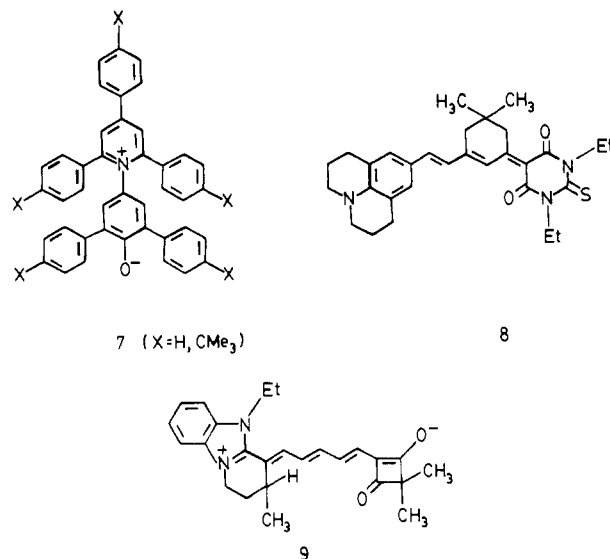


The following presentation gives a short account of the solvatochromic behavior of these solutes, especially the influence of the azo moiety toward solvatochromism, and of the π_{azo}^* scale, which is derived from the spectral characteristics of these solutes in different solvents. Comparison with other solvent polarity scales, especially the π^* scale, is included in the discussion.

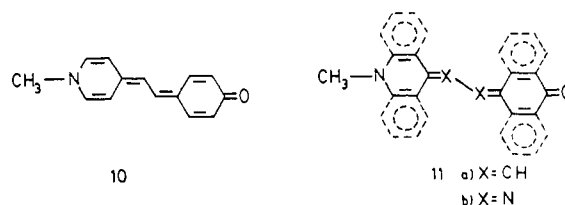
Solvatochromic Indicators

Kosower, in 1958, was the first to systematically use solvatochromism as a probe of solvent polarity.¹⁴ Later, Dimroth and Reichardt utilized the merocyanine 7, X = H, as a solvatochromic dye.¹⁵ Recently its pentatert-butyl derivative, X = C(CH₃)₃, was reported to be ideal due to its improved solubility in a greater range of solvents, and the pronounced solvent sensitivity of its most bathochromic absorption band.¹⁶ Brooker reported χ_R and χ_B scales based on the π - π^* transition energies of two meropolymethine dyes, 8 and 9.¹⁷

An early report by Hünig and co-workers¹⁸ on the solvatochromism of merocyanines and azo merocyanines received only scant attention.^{10,19} They investigated merocyanines of the type 10 as well as 11a and 11b with different numbers of fused rings. A reverse solvatochromism was observed with azo merocyanines 11a,b in pyridine-water mixtures, which was rationalized by



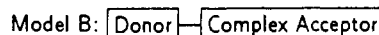
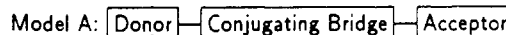
the reversal of refractive index and dielectric constant with increasing solvent polarity. A reverse solvatochromism was predicted by semiempirical MO methods for the merocyanine dye 10.²⁰ Recently, Jacques confirmed this prediction with experimental evidence showing that a reversal actually occurred.²¹



Influence of Azo Group on the Solvatochromism of Merocyanines.

Studies on solvatochromism of merocyanines have mostly focused on stilbazolium type dyes.^{11,17,20,22-24} Reports of spectral data of azo merocyanines in various solvents are fairly limited. However, recently we have studied the solvatochromic behavior of azo merocyanines 1-6 in 29 different solvents²⁵ and found a reverse solvatochromism, which is discussed further subsequently. In this connection, a brief account of the influence of the azo group on the solvatochromism of merocyanines is given below.

The special properties of merocyanines are based on donor-acceptor chromogens. Generally, the donor (D) and acceptor (A) chromogens can be viewed in two ways:²⁶



In model A, the conjugating bridge merely serves as a connecting bridge to extend the conjugation of a system, e.g., 12. In model B, the complex acceptor unit is expected to accept the negative charge and provide the extra conjugation as well, e.g., 13.

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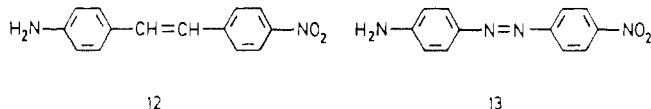
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Table I
Summary of the Properties of the Three Main Types of Merocyanine Dyes²⁶

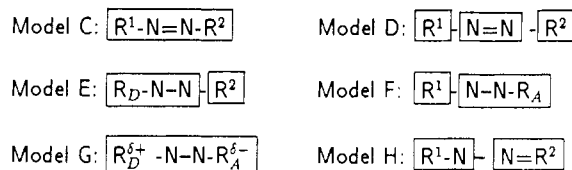
type	ground state		excited state		solvent-induced shift
	polarity	bond length alternatn	polarity	bond length alternatn	
weakly dipolar	low	high	increased	reduced	bathochromic
moderately dipolar	medium	low	little change	little change	
highly dipolar	high	high	reduced	reduced	hypsochromic

In **12**, the donor group (NH₂) and the simple acceptor (NO₂) are linked by the stilbene bridge, which merely provides a conjugated pathway between D and A. In contrast, in the iso- π -electronic molecule **13**, the nitro-



gen atoms of the azobenzene bridging unit are powerful acceptors and contribute to the development of color compared to the central carbon atoms in **12**. The same argument could be extended to heterocyclic azo dyes, an area where published spectral data is still limited.

Fabian and Hartmann classify azo merocyanines in the following manner:²⁷



Model C treats the π -electron structure as one unit, which enables common characteristics to be revealed between azo and stilbene dyes, as they are isoelectronic to each other. Model D fragments the compound into three subunits: R₁, R₂, and the central -N=N- group, similar to model A. Models E and F are based on the assumption that one of the moieties, R₁ or R₂, may display marked donor (R_D) or marked acceptor (R_A) properties. The azo group is said to manifest an acceptor property. Model G regards R₁ and R₂ as strong donor and acceptor groups. Model H complements model C, wherein the azo group is fragmented. On the basis of the above classification of azo dyes, compound **1** could be included under model F, i.e., the azo acceptor part of the molecule is considered as a unified acceptor unit.

It has long been known that solvent effects depend largely on differing dipolar characteristics of a molecule when it is promoted to the excited state. Depending on the change in the dipolar characteristics between ground and excited states, three possibilities exist, as shown in Table I.²⁶

In view of the above discussion, and also from the theoretical work on dye **10** by Benson and Murrell,²⁰ it is inferred that **10** is classified as a moderately dipolar dye in relatively nonpolar solvents, whereas in a strongly polar medium it is regarded as a highly dipolar dye. The reverse solvatochromism arises from a possible change in the electronic configuration, i.e., from the quinoidal form to the benzenoid structure. Botrel et al. have shown that the calculated dipole moments exhibit the following evolution: $\mu_g < \mu_e$ in less polar

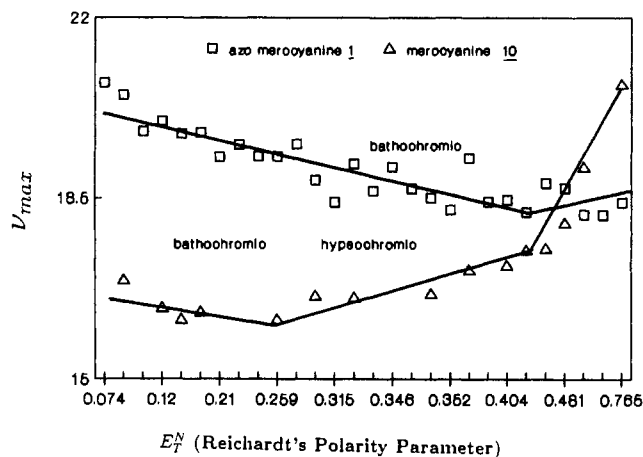


Figure 1. Plot showing the reverse solvatochromism in **1** and **10** at different regions of solvent polarity.

solvents, and $\mu_g > \mu_e$ in highly polar solvents.²⁸

The effect of structural change, on replacement of the -CH=CH- bridge by -N=N-, is seen through comparison of the plots of spectral data for **10** and **1** vs the E_T^N parameters. The trends observed are shown in Figure 1, from which the following features are seen:

(a) Merocyanine dye **10** exhibits a *bathochromic* shift in nonpolar solvents ($E_T^N = 0.0-0.26$). This suggests that **10** is a weakly dipolar dye.

(b) Dye **10** reverses its solvatochromic property in the region of higher solvent polarity ($E_T^N \geq 0.26$) and displays a *hypsochromic* shift, characteristic of a highly dipolar dye.

(c) In contrast, the azo merocyanine **1** exhibits a *bathochromic* shift in the solvent polarity region $E_T^N = 0-0.41$; this is characteristic of a weakly dipolar dye.

(d) Dye **1** displays a slight reversal in its solvatochromic behavior in the region $E_T^N = 0.41-0.80$, characteristic of a moderately dipolar dye.

Figure 1 is very meaningful as it shows the complete range of spectral response of merocyanine dyes, as the -C=C- linkage is replaced by a -N=N- moiety, i.e., weakly dipolar \rightarrow

moderately dipolar (azo merocyanine, **1**)

weakly dipolar \rightarrow moderately dipolar \rightarrow

highly dipolar (merocyanine, **10**)

This would also provide an answer to the query raised by Griffiths, viz., "The 1,2-diazamerocyanines are unusual in showing no evidence of hypsochromic shifts in polar solvents, even for structures such as **1**, which are highly polar merocyanines."²⁶ Clearly, that conclusion was drawn on the basis of insufficient data.

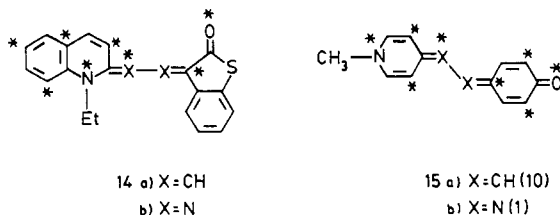
The azo merocyanine **1** is not a highly dipolar dye, rather it is a weakly dipolar dye in the region $E_T^N = 0-0.6$, slowly tending toward moderately dipolar in more polar solvents with $E_T^N = 0.6$. Hence it does not show

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strongly hypsochromic shifts as would have been expected. A similar trend is observed for dyes 2–6.

Secondly, from Figure 1, it is seen that 1 absorbs at shorter wavelengths than does its carbon analogue 10. Such a trend has been reported earlier by Glauert and Mann for dye 14, X = CH, $\lambda_{\max}^{\text{MeOH}}$ 554 nm; X = N, $\lambda_{\max}^{\text{EtOH}}$ 454 nm.²⁹



This kind of behavior has been rationalized by using perturbational theory.²⁶ According to Dewar's rules, an electronegative hetero atom or an electron-withdrawing group placed at the central starred atom in 14 should give a hypsochromic shift. This reasoning can be extended to 1. However, the opposing spectral effects at the conjugating bridge containing the -N=N- group at the starred and unstarred positions are not equal. This could possibly lead to hypsochromic shifts compared to its carbon analogue. This hypsochromic shift resulting from the structural change 14a → 14b or 15a → 15b should not be confused with the hypsochromic shift arising from varying solvent polarity. Thirdly, it is seen that the extent of shifts for 10 is considerably larger than for 1.

Solvent Polarity Scales

A number of scales have been established to quantify the influence of solvent on chemical properties. These scales are based on some physicochemical property, which could be an equilibrium constant, reaction rate constant, spectral shift using absorption spectroscopy, etc. The scales have been designed by using two main approaches: the single-parameter approach and the multiple-parameter approach, as discussed below.

Single-Parameter Approach. In the single-parameter approach, empirical polarity scales are correlated with various physicochemical processes. These processes comprise (a) equilibrium measurements such as D_1 ,³⁰ $K_{o/w}$ and π_x ,³¹ and D_N ,³² (b) kinetic measurements such as Y ,³³ $\log k_1$,³⁴ $\log k_2$,³⁵ X ,³⁶ and Ω ,³⁷ (c) spectroscopic measurements such as Z ,¹⁴ E_T ,¹⁵ S ,³⁸ G ,³⁹ A_N ,⁴⁰

Py,⁴¹ χ_R and χ_B ,¹⁷ and (d) other measurements including D_{ce} and δ .¹⁰ Recently Reichardt converted the E_T scale based on dye 7 into the dimensionless E_T^N scale.¹⁶

In applying these solvent polarity scales based on a single parameter, it should be borne in mind that it is tacitly assumed that solvation resulting from a complex combination of solute-solvent interactions between the solvent and the reference substrate is the same as with the particular substrate under consideration. This aspect has been found to be an oversimplification, as this approach does not account for various observations and measurements such as kinetic, spectroscopic, etc., involving diverse solute-solute interactions.

Multiparameter Approach. Due to the lack of precision and generality in the single-parameter approach, a series of multiparameter equations have been proposed to delineate specific and nonspecific solute-solvent interactions. This approach takes into account two or more aspects of solvation in the general form expressed in eq 1,

$$A = A_0 + yY + pP + eE + bB \quad (1)$$

where A is the value of some physicochemical property in a series of solvents, and A_0 is the corresponding quantity for the gas phase or for an inert solvent taken as the reference state. Y is the solvent polarization; P is the solvent polarizability; E is the Lewis acidity; B is the Lewis basicity, and the constants y , p , e , and b indicate the relative contributions of these parameters.⁴² Other multiparameter approaches have also been reported.^{43,44}

Among the various scales proposed in the past, the π^* scale from the Kamlet, Abboud, Taft, and Abraham group deserves special recognition. It is based on the averaged spectral behavior of a number of solutes, rather than on the spectral data of any single compound, so as to correct inherent spectral anomalies from choosing a single solute. The solvatochromic comparison method (SCM) was introduced⁴⁵ in order to account for specific and nonspecific interactions. Thus their approach, extended to include a solubility parameter, links microscopic and macroscopic quantities.

Many solubility and solvent-dependent properties represented by the term XYZ (similar to A in eq 1) can be expressed in terms of a linear combination of three types of terms as shown in eq 2. The cavity term is $XYZ = (XYZ)_0 + \text{cavity term} + \text{dipolar term} + \text{hydrogen-bonding term(s)}$ (2)

said to measure the free energy or enthalpy input necessary to separate the solvent molecules; the dipolar term (dependent on exoergic interactions of the solvent and solute) measures the effects of solute-solvent, dipole-dipole, and dipole-induced dipole interactions; the hydrogen-bonding terms are expected to reflect the

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exoergic effects of complexation between HBD solvents and HBA solutes measured by α_1 and β_2 .^{19,45-47}

When one includes the solvatochromic parameters, eq 3 is obtained, where subscript 1 refers to the solvent and subscript 2 to the solute. Considering only the case $XYZ = (XYZ)_0 + A(\delta_H^2)_1 V_2/100 + B\pi_1^* \pi_2^* + C\alpha_1(\beta_m)_2 + D\beta_1(\alpha_m)_2$ (3)

of a single solute in a series of solvents, all the solute parameters are constant. In view of the varying polarizable influence of diverse families of solvents, a polarizability correction term δ has been introduced, and the solvatochromic equation takes the form as in eq 4,⁴⁵

$$XYZ = (XYZ)_0 + s(\pi^* + d\delta) + a\alpha + b\beta + h(\delta_H^2) \quad (4)$$

where π^* is a measure of solvent dipolarity/polarizability, δ_H denotes the Hildebrand solubility parameter, and s , a , b , and h are solvatochromic coefficients.

This approach has been found to be significant as it delineates dipolarity/polarizability and hydrogen-bonding interactions. The α and β scales give a quantitative measure of hydrogen-bonding capabilities of different solvents. In formulation of the π^* scale, Taft and co-workers classified the solvents on the basis of hydrogen-bonding capabilities as non-hydrogen-bonding (NHB), hydrogen-bond-acceptor (HBA), hydrogen-bond-donor (HBD), and amphiprotic (HBA-HBD) solvents. They chose seven primary solutes consisting of mainly nitro aromatic compounds. The spectral data of these primary solutes in select solvents (NHB) were treated in a "Round Robin parameter optimization program" to arrive at a set of 28 π^* values which were consistent with $\pi^* = 0.00$ for cyclohexane and $\pi^* = 1.00$ for dimethyl sulfoxide. Subsequently using the equation $\pi_i^* = \nu_{\max} - \nu_0/s$, further π_i^* values for additional solvents were obtained.^{19,45}

A Decade of the π^* Scale. Since the introduction of the π^* scale in 1977, and of the SCM, this scale has risen up the ladder of polarity scales. However, Swain and co-workers formulated two new solvent polarity scales, A (acity) and B (basity), as counter scales to Kamlet and Taft's approach. Swain's scales are based on an extensive computational procedure involving over 1000 data sets for 61 solvents and 77 physicochemical properties.⁴⁴ This approach has received only limited attention. Bekárek attempted to modify the π^* , α , and β scales by dividing them by the refractive index.⁴⁸ This was intended to correlate most types of solvent properties. However, this attempt was discouraged, on the basis that the improvements were not significant.⁴⁹ This was followed by Swain's rebuttal in 1984.⁵⁰ A new thermosolvatochromic comparison method advocated by Laurence et al. attempts to improve the SCM, particularly due to the insufficiently precisely determined solvatochromic parameters.⁵¹ It is argued that the ν_{\max}

values determined by Kamlet et al. do not accommodate temperature dependence. Laurence et al. have derived new solvent dipolarity/polarizability and β parameters based on the corrections used in the thermosolvatochromic method.⁵¹ Carr et al. have shown that a single parameter π^* is not adequate to describe the dipolarity and polarizability.⁵² Sjöström and Wold have recommended the use of π_o^* and π_d^* as substitutes for π^* . The π_o^* and π_d^* parameters are supposed to represent solvent orientational and distortional polarizability scales.⁵³

There is considerable controversy as to the nature of linear solvation energy relationships (LSERs), whether they represent empirical generalizations or fundamental rules.⁵⁴ Though the controversy remains unresolved, it may be inferred that, from a rigorous mathematical point of view, LSERs are local empirical rules according to Wold and Sjöström, whereas from a more practical view, they could be considered as fundamental relationships of chemistry.

The π_{azo}^* Scale of Solvent Polarity

Though more than a decade has passed since the introduction of the π^* scale, there have been no reported attempts to formulate an alternative scale based on a different set of solutes. Examination of the primary set of solutes chosen by Kamlet's group raises questions on the true generality of the scale, as it is based on a primary set consisting mainly of nitro aromatic compounds. In order to reexamine the basic tenets of the solvatochromic comparison method, we decided to formulate a new scale based on the spectral data of six novel azo merocyanines. As noted earlier, merocyanine dyes are one of the important classes of compounds due to their special biological, chromogenic, and technological properties. A new scale, called the π_{azo}^* scale, has been formulated by optimizing spectral data of the six azo merocyanines 1-6 which were consistent with $\pi_{\text{azo}}^* = 0.00$ for cyclohexane and $\pi_{\text{azo}}^* = 1.00$ for dimethyl sulfoxide.²⁵

We found that the response of azo merocyanines to the dipolarity/polarizability component of solvent properties varies only in degree in comparison with the nitro aromatics used in Kamlet's work. As may have been expected, the following correlations show that the π_{azo}^* scale based on azo merocyanines correlates better with (a) scales based on structurally similar dyes and (b) dyes that are structurally similar to azo merocyanines. It is interesting, however, that the π_{azo}^* scale apparently provides an overall better criterion of solute-solvent behavior than does π^* according to the quality of the correlations described below.

Correlation with Various Dyes. When the spectral data of 59 different solutes selected from a broad range of compounds was correlated with the π^* and π_{azo}^* scales, linear correlations were obtained. The standard deviations σ vary from 0.110 to 1.56 for the π^* scale and from 0.090 to 1.10 for the π_{azo}^* scale. The correlations showed that the π_{azo}^* scale is better than the π^* scale when one considers groups of compounds such as the azo merocyanine dyes (1-6), Dimroth and Reichardt's as well as Brooker's merocyanine, Nile blues A and B (19, 20), 7,7'-disubstituted quinone methides (24-31),

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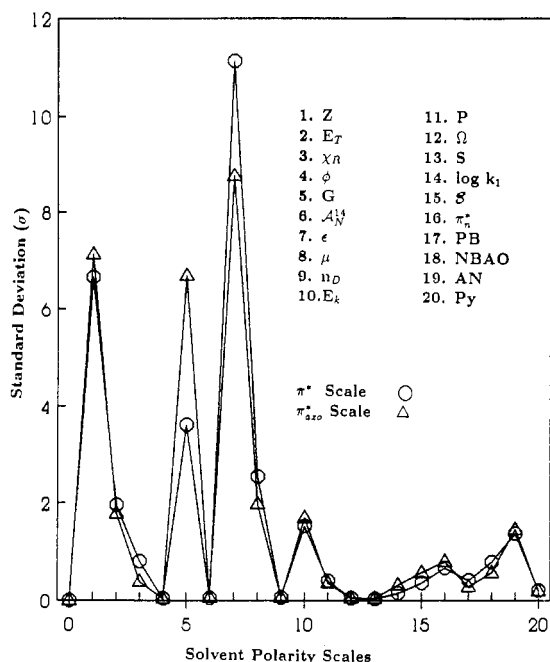


Figure 2. Plot of standard deviation (σ) vs solvent polarity scales.

azobenzenes (40–49), and Figueras's phenol blues (56–59). At the same time, the π^* scale is better than the π^*_{azo} scale for nitro aromatic compounds (7–10 and 30–39).²⁵

Correlation with Various Scales. Among the various scales in the literature, 20 scales were chosen wherein data was available for more than five solvents to examine correlations with the π^* and π^*_{azo} scales. The σ values obtained from these correlations are plotted against the different scales in Figure 2. It is seen that the π^*_{azo} scale correlates well overall but especially so for scales based on merocyanine dyes such as Brooker's χ_R scale and Reichardt's E_T .

Present Status of Polarity Scales

The interrelation between various scales and a generalized summary of solvent polarity scales is given in the excellent review by Reichardt.¹⁰ Of the solvent polarity scales derived from various physicochemical processes, the most comprehensive are those based on the solvatochromic method. Of the 30-plus solvent polarity scales presently known, about 10 have found the majority of applications in the correlation analysis of solvent effects. Also Reichardt's scale, i.e., E_T^N (E_T as well), has been found to encompass the largest number of solvents. If one compares the various scales, one finds, surprisingly, that most of these agree with each other qualitatively. However, even though the single-parameter approach has been known to serve as

a general approximation of solvent polarity, it is fairly inadequate in correlating a number of solvent-sensitive processes. It would be an overzealous expectation to be able to obtain a universally determinable solvent polarity scale using a single-parameter approach. Limitations are also found in the multiparameter approaches such as those of Kamlet et al. and Swain et al. The solvent parameters such as α , β , π^* (Kamlet), and A_j and B_j (Swain) have been criticized as having been obtained by statistically optimized procedures. In addition, the separation of solvent effects into various additive contributions may be considered to be somewhat arbitrary, since different solute/solvent interaction mechanisms can operate differently.

In spite of the limitations or inherent weaknesses, from a physical organic chemist's point of view, the multiparameter approach is certainly a positive and meaningful pathway. Though arbitrary, the separation of solvent parameters in terms such as hydrogen-bond donor and hydrogen-bond acceptor, in addition to polarizability and dipolarity, is very meaningful in analyzing solvent effects. The averaging of solvent parameters from a number of solutes has been found useful so as to avoid skewing effects that might arise from using any one solute. However, a criticism that can be put forward concerning solvent polarity scales based on the multiparameter approach is that the range of substrates chosen for study have not been representative of a sufficiently wide variation in structure. Hence the establishment of a universal solvent polarity scale remains to be realized in the future.²⁵

Finally, in the context of solvent polarity scales, it may be of interest to requote Karl Popper: "It is always undesirable to make an effort to increase precision for its own sake...since this usually leads to loss of clarity.... One should never try to be more precise than the situation demands.... Every increase in clarity is of intellectual value in itself; an increase in precision or exactness has only a pragmatic value as a means to some definite end."^{10,55}

Our research in the area of azo, azoxy, and merocyanine dyes, and of medium effects on reaction rates on equilibria, has been supported over the years by the Natural Sciences and Engineering Research Council of Canada. The outstanding efforts of our co-workers, quoted in the cited literature, have been largely responsible for whatever contributions we have been able to make in this area. Part of this Account was written during the sabbatical leave of E.B. at the Université Pierre et Marie Curie (Paris VI). The hospitality of Professors R. Schaal and F. Terrier is warmly acknowledged.

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