

Solvatochromic Dyes as Solvent Polarity Indicators

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Contents

I. Scope	2319
II. Introduction	2319
III. Linear Free-Energy Relationships	2321
IV. Solvatochromism	2322
A. Solvent Effects on UV/Vis/Near-IR Absorption Spectra	2322
B. Solvatochromic Compounds	2323
V. Empirical Parameters of Solvent Polarity from UV/Vis/Near-IR Spectroscopic Measurements	2323
A. Single Parameter Approaches	2323
B. The $E_T(30)$ and E_T^N Scale of Solvent Polarity	2334
C. Multiparameter Approaches	2346
VI. Interrelation between Empirical Solvent Polarity Parameters	2349
VII. Summary and Conclusions	2352
VIII. Acknowledgments	2353
IX. References	2353

I. Scope

This review compiles positively and negatively solvatochromic compounds which have been used to establish empirical scales of solvent polarity by means of UV/vis/near-IR spectroscopic measurements in solution—with particular emphasis on the $E_T(30)$ scale derived from negatively solvatochromic pyridinium *N*-phenolate betaine dyes.

This requires a short discussion of the concept of solvent polarity and how empirical parameters of solvent polarity can be derived and understood in the framework of linear free-energy relationships. The preconditions for the occurrence of solvatochromism, and further requirements of solvatochromic compounds for them to be useful as solvent polarity indicators will be discussed. In addition to spectroscopically based single parameters of solvent polarity, multiparameter treatments of solvent effects by means of solvatochromic parameters will also be mentioned.

The mutual interrelation between some of the more important UV/vis/near-IR spectroscopically derived solvent scales, and their correlations with solvatochromic multiparameter equations will be exemplarily given.

II. Introduction

Rates and equilibrium positions of chemical reactions, as well as the position and intensity of absorption bands in UV/vis/near-IR, IR, NMR, and ESR spectroscopy, are solvent-dependent.^{1–15} Nowadays, this is generally known to every chemist, and the



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careful selection of an appropriate solvent for a reaction or absorption under study is part of its craftsmen’s skill. The influence of solvents on the rates of chemical reactions was first noted by Berthelot and Péan de Saint-Gilles in 1862 in connection with their studies on esterification of acetic acid with ethanol (“The esterification is disturbed and decelerated on addition of neutral solvents not belonging to the reaction”)¹⁶ and followed by the pioneering work of Menshutkin in 1890 on the alkylation of tertiary amines with haloalkanes.^{17,18} Menshutkin’s statement that “a chemical reaction cannot be separated from the medium in which it is performed” still remains valid—and has recently been more casually expressed as “In searching to understand the rate of a reaction in solution, the baby must not be separated from its bath water”.¹⁹

The influence of solvents on the position of chemical equilibria was discovered in 1896 by Claisen,²⁰ Knorr,²¹ and Wislicenus²² independently of each other, simultaneously with the discovery of keto–enol tautomerism in 1,3-dicarbonyl compounds. Claisen wrote, “...It depends on the nature of substituents, the temperature, and for dissolved compounds, also on the nature of the solvent, which of the two forms

(i.e. keto and enol form) will be the more stable."²² These results were first reviewed by Stobbe in 1903,²³ who divided the solvents used into two groups according to their ability to isomerize tautomeric compounds. To some extent, his classification reflects the modern division of solvents into hydrogen-bond donor (HBD, protic) solvents and non-hydrogen-bond donor (non-HBD, aprotic) solvents.

In contrast to these more historical investigations, a few recent examples from different areas shall demonstrate the powerful influence of solvents on chemical reactions and spectral absorptions:

(a) The equilibrium constant of the 1:1 complex formed between a macrobicyclic cyclophane receptor and pyrene varies by a factor of ca. 10^6 upon changing the solvent from carbon disulfide to water, which corresponds to a solvent-induced difference in the Gibbs binding energy of $\Delta\Delta G^\circ = 8.1$ kcal/mol.^{24,25}

(b) Comparison of the unimolecular heterolysis rate constants of 2-chloro-2-methylpropane obtained in benzene and in water reveals a rate acceleration of ca. 10^{11} with increasing solvent polarity.^{26,27} The first-order rate constant of the decarboxylation of 6-nitrobenzoxazole-3-carboxylate varies by up to 8 orders of magnitude on going from reaction in hexamethylphosphoric triamide to reaction in water.^{28,29}

(c) The intramolecular charge-transfer UV/vis/near-IR absorption band of the solvatochromic 2,6-diphenyl(2,4,6-triphenyl-1-pyridinio)phenolate betaine dye **36** is shifted from $\lambda_{\max} = 810$ nm to $\lambda_{\max} = 453$ nm ($\Delta\lambda = 357$ nm, $\Delta\tilde{\nu} = 9730$ cm⁻¹) on going from diphenyl ether to water as solvent.¹ This corresponds to a solvent-induced change in excitation energy of ca. 28 kcal/mol.

(d) In the fluorescence spectrum of 1-phenyl-4-[(4-cyano-1-naphthyl)methylene]piperidine (**71**), the emission maximum is shifted from $\lambda_{\max} = 407$ nm to $\lambda_{\max} = 694$ nm ($\Delta\lambda = 287$ nm, $\Delta\tilde{\nu} = 10200$ cm⁻¹) by changing the solvent from *n*-hexane to acetonitrile.³⁰

(e) The solvent-induced IR frequency shift for the C=O stretching vibration of tetramethylurea is $\Delta\tilde{\nu} = 71$ cm⁻¹ in going from *n*-hexane ($\tilde{\nu} = 1656$ cm⁻¹) to water ($\tilde{\nu} = 1585$ cm⁻¹) as solvent.³¹ Corresponding solvent effects on the IR spectra of ethyl acetate [$\tilde{\nu}(\text{C=O})$] and acetonitrile [$\tilde{\nu}(\text{C}\equiv\text{N})$] have been very recently obtained.^{32,33}

(f) The solvent-induced difference in the ³¹P NMR chemical shift of triethylphosphane oxide, measured in *n*-hexane and in water, is $\Delta\delta \approx 23$ ppm.^{34,35} Even the NMR chemical shift of the nonpolar solute ¹²⁹Xe can vary by up to $\Delta\delta = 200$ ppm depending on the solvent used.^{36,37}

(g) The nitrogen and hydrogen hyperfine splitting constants, as well as the spin densities on the nitrogen and carbon atoms, taken from the ESR spectrum of the 2-[4-(dimethylamino)phenyl]indan-1,3-dionyl radical, are highly solvent-dependent.³⁸ Similar solvent effects on ESR spectra have also been found recently with paramagnetic organometallic complexes such as Co(CO)₃L₂ (L = chelating phosphane).³⁹

Responsible for all these medium effects is the *differential solvation* of (i) reactants and products (\rightarrow position of chemical equilibria); (ii) reactants and activated complexes (\rightarrow rates of chemical reactions);

or (iii) molecules in the corresponding ground and excited states (\rightarrow physical absorption of electromagnetic radiation). The extent of this differential solvation depends on the *intermolecular forces* between solute and surrounding solvent molecules. Intermolecular forces include nonspecific forces such as purely *electrostatic forces* arising from the Coulomb forces between charged ions and dipolar molecules [i.e. ion/ion, ion/dipole, dipole/dipole] and *polarization forces* that arise from dipole moments induced in molecules by nearby ions or dipolar molecules [i.e. ion/nonpolar molecule, dipole/nondipolar molecule, two nonpolar molecules (dispersion energy)], as well as specific forces such as hydrogen-bonding between HBD and HBA ions or molecules, and electron-pair donor (EPD)/electron-pair acceptor (EPA) forces.⁴⁰⁻⁴² Obviously, intermolecular solute/solvent interactions are of highly complicated nature and difficult to determine quantitatively.

Chemists have tried to understand solvent effects on chemical reactions in terms of the so-called *solvent polarity*, which is not easy to define and to express quantitatively. What does solvent polarity mean? The simplicity of idealized electrostatic models for the description of solvation of ions and dipolar molecules, considering solvents as nonstructured continuum, has led to the use of physical constants, such as static dielectric constant (ϵ_r), permanent dipole moment (μ), refractive index (n), or functions thereof, as macroscopic solvent parameters for the evaluation of medium effects. However, solute/solvent interactions take place on a molecular microscopic level within a structured discontinuum consisting of individual solvent molecules, capable of mutual solvent/solvent interactions. For this reason, and because of neglecting specific solute/solvent interactions, the electrostatic approach to medium effects often failed in correlating observed solvent effects with physical solvent parameters.¹ In reality, satisfactory quantitative descriptions of medium effects have to take into account all nonspecific and specific solute/solvent, solvent/solvent and, at higher concentrations, even solute/solute interactions. Therefore, from a more pragmatic point of view, it seems to be more favorable to define "solvent polarity" simply as the overall solvation capability (or solvation power) of solvents, which in turn depends on the action of all possible, nonspecific and specific, intermolecular interactions between solute ions or molecules and solvent molecules, excluding, however, those interactions leading to definite chemical alterations of the ions or molecules of the solute (such as protonation, oxidation, reduction, chemical complex formation, etc.). This definition of solvent polarity was given in 1965,^{1,43} and it seems to be becoming more and more accepted by the scientific community.⁴⁴⁻⁴⁶

Apparently, solvent polarity thus defined cannot be described quantitatively by single physical solvent parameters such as dielectric constants, dipole moments, etc. The lack of comprehensive theoretical expressions for the calculation or prediction of solvent effects on chemical reactivity, and the inadequacy of defining solvent polarity in terms of simple physical solvent characteristics, have led to the introduction of so-called *empirical parameters of solvent polar-*

ity.^{1,43,47} On the basis of the assumption that particular, carefully selected, well-understood and strongly solvent-dependent chemical reactions or spectral absorptions may serve as suitable model processes for recording medium effects; various empirical solvent polarity scales have been developed this way.^{1,47}

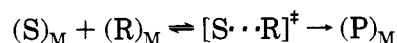
The desmotropic constant, L , introduced by Meyer in 1914 as a measure of the enolization power of solvents for 1,3-dicarbonyl compounds, can be considered as the first empirically determined solvent parameter, using the keto-enol tautomerization of ethyl acetoacetate as the solvent-dependent reference process.⁴⁸ However, the first real empirical parameter of "solvent ionizing power" was the Y scale introduced by Winstein et al. in 1948, derived from the S_N1 heterolysis of 2-chloro-2-methylpropane.^{47g,49} The first suggestion that solvatochromic dyes could serve as visual indicators of solvent polarity was made by Brooker et al. (from the Eastman Kodak Company in Rochester, NY) in 1951,⁵⁰ but Kosower was the first to set up a real spectroscopic solvent polarity scale in 1958. This was called the Z scale and used the intermolecular charge-transfer (CT) absorption of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide as the solvent-sensitive reference process.^{3,44,51} Since then, various additional UV/vis/near-IR-based solvent polarity scales have been developed, using negatively or positively solvatochromic dyes of different chemical structure, and, depending on their structure, capable of registering all or only selected types of intermolecular dye(solute)/solvent interactions.^{1,47} The main aim of this paper is to collect these solvatochromically derived solvent polarity scales and to compare them with respect to their usefulness.

In applying such single-parameter solvent scales, it is tacitly assumed that the combination of solute/solvent interactions between the reference solute(s) and the solvent is almost the same as with the particular substrate under consideration. Obviously, this is an oversimplification which causes serious limitations of the single-parameter approach to medium effects. Therefore, more recently, multiparameter correlation equations have been developed, which consist of up to four single empirical parameters, each of them measuring a certain aspect of the overall solvation capability of a given solvent (e.g. solvent polarizability, dipolarity, Lewis acidity, and Lewis basicity).^{1,47a,b,f,52,53} If the one-parameter approach for correlating solvent effects fails, then multiparameter correlations come into play.

This method of proceeding, i.e. the use of reference or standard compounds in order to establish empirical solvent polarity parameters, is quite common in chemistry and takes usually the form of a linear free-energy (LFE) relationship.⁵⁴⁻⁵⁷

III. Linear Free-Energy Relationships

LFE relationships involve empirical relationships between rates or equilibria of chemical reactions, which show some similarity within a so-called reaction series. Considering a chemical reaction between a substrate S and a reagent R in a medium M , which leads, via an activated complex, to the product(s) P , according to



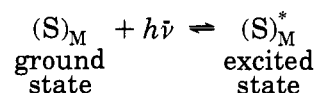
there are three possibilities of introducing small changes in order to establish a reaction series:^{1,54-57}

(a) First, one can change the substrate by introducing different substituents. This leads, particularly in case of meta- and para-substituted benzene derivatives, to the well-known Hammett equation.⁵⁸ A recent, typical example of this kind of LFE relationship is the substituent-dependent alkylation of pyridinium N -phenolate betaine dyes.^{59,60}

(b) Second, one can change the reagent (equal to catalyst). This gives, e.g. in case of acid- or base-catalyzed reactions, the famous Brønsted-Pedersen equation, which establishes a LFE relationship between the strength of acids or bases and their effectiveness as catalysts.⁶¹ This catalysis equation, first introduced in 1924, was the first LFE relationship.

(c) Third, in order to obtain a reaction series, one can change the surrounding medium, while leaving all other reaction partners unchanged. In the case of sufficiently solvent-dependent chemical reactions, this leads to kinetically derived empirical parameters of solvent polarity, such as the Y values of Winstein.⁴⁹

A simple modification to the previous equation, by replacing the reagent R with photons $h\nu$ and the product P with the substrate S in the spectroscopically excited state, leads to



This replacement now corresponds to an extension of the LFE principle, as applied to reaction series, to so-called absorption series, which are available in all areas of absorption spectroscopy (UV/vis/near-IR, IR, ESR, NMR). In order to establish an absorption series, there are two possibilities to alter the parameters of this equation:

(a) First, one can again change the substrate by introducing different substituents. This leads to spectroscopically derived Hammett equations connecting substituent-induced wavenumber shifts of suitably substituted substrates with Hammett substituent constants. Examples of Hammett relationships for UV/vis spectroscopic data can be found in the literature.^{62,63}

(b) Second, only the medium in which the substrate is to be dissolved is changed. Provided the position of the spectral absorption band of the substrate is sufficiently solvent dependent, this procedure can be used to establish spectroscopically derived scales of solvent polarity, as described in this paper for UV/vis/near-IR absorptions. That is, solvent polarity scales as derived by means of absorption spectroscopy and their applications are, in principle, further examples of LFE relationships.^{1,54-57} However, the important question of whether LFE relationships are fundamental laws of chemistry,⁶⁴ or only locally valid, empirical rules,⁶⁵ is still a matter of debate.

IV. Solvatochromism

A. Solvent Effects on UV/Vis/Near-IR Absorption Spectra

It has long been known that UV/vis/near-IR absorption spectra of chemical compounds may be influenced by the surrounding medium and that solvents can bring about a change in the position, intensity, and shape of absorption bands.^{66–68} Hantzschlater termed this phenomenon *solvatochromism*.⁶⁹ However, the now generally accepted meaning of the term *solvatochromism* differs from that introduced by Hantzsch.¹ One of the referees has recommended to replace *solvatochromism* by the term *perichromism* (from Greek *peri* = around) in order to stress that spectroscopic probe molecules cannot only measure the polarity of liquid environments, but also that of solids, glasses, and surfaces. The term *solvatochromism* is, however, so well established in the literature that it would be difficult to convince the scientific community to change this term to *perichromism*, which is certainly a more general expression for the spectroscopic phenomena under consideration.

A hypsochromic (or blue) shift of the UV/vis/near-IR absorption band, with increasing solvent polarity is usually called “negative solvatochromism”. The corresponding bathochromic (or red) shift, with increasing solvent polarity, is termed “positive solvatochromism”. Obviously, solvatochromism is caused by differential solvation of the ground and first excited state of the light-absorbing molecule (or its chromophore): if, with increasing solvent polarity, the ground-state molecule is better stabilized by solvation than the molecule in the excited state, negative solvatochromism will result. Or vice versa, better stabilization of the molecule in the first excited state relative to that in the ground state, with increasing solvent polarity, will lead to positive solvatochromism. In this context, “first excited state” means the so-called Franck–Condon excited state with the solvation pattern present in the ground state.

Since the time required for a molecule to get electronically excited (about 10^{-15} s) is much shorter than that required to execute vibrations or rotations (about 10^{-12} to 10^{-10} s), the nuclei of the absorbing entity (i.e. absorbing molecule + solvation shell) do not appreciably alter their positions during an electronic transition (Franck–Condon principle).⁷⁰ Therefore, the first excited state of a molecule in solution has the same solvation pattern as the corresponding ground state and is called Franck–Condon excited state, whereas the ground state corresponds to an equilibrium ground state. If the lifetime of the excited molecule is large enough, then reorientation of the solvent molecules, according to the new excited situation, takes place, and a relaxed excited state with a solvent shell in equilibrium with this state results. It is from this equilibrium excited state that fluorescence can occur. By analogy, there is a Franck–Condon ground state after emission with the solvation pattern of the equilibrium excited state, which persists briefly until the solvent molecules reorganize to the equilibrium ground state. The

differential solvation of these two states is responsible for the solvent influence on emission or fluorescence spectra. The solvent dependence of the position of emission bands in fluorescence spectra has been often included in the term *solvatochromism*.¹ The solvent dependence of fluorescence spectra has been sometimes called *solvatofluorochromism*⁷¹ or *fluorosolvatochromism*.⁷² However, because of the close connection between spectral absorption and emission, there is no need for special terms for fluorescence-based solvatochromism.

The solvatochromism observed depends on the chemical structure and physical properties of the chromophore and the solvent molecules, which, for their part, determine the strength of the intermolecular solute/solvent interactions in the equilibrium ground state and the Franck–Condon excited state. This is not the place to discuss the relation between extent and sign of solvatochromism and the structure of solvatochromic dyes; the reader is referred to recent reviews.^{1,73–80} In general, dye molecules with a large change in their permanent dipole moment upon excitation exhibit a strong solvatochromism. If the solute dipole moment increases during the electronic transition ($\mu_g < \mu_e$), a positive solvatochromism normally results. In the case of a decrease of the solute dipole moment upon excitation ($\mu_g > \mu_e$), a negative solvatochromism is usually observed. Solutes with this particular solvatochromic behavior can be commonly found among so-called meropolymethine dyes (particularly among merocyanine dyes = vinylogous amides) and among compounds with inter- or intramolecular CT absorptions.^{1,73,77,78} In addition to the dipole moment change on excitation, the ability of a solute to donate or to accept hydrogen bonds to or from surrounding solvent molecules in its ground and Franck–Condon excited state determines further the extent and sign of its solvatochromism.^{81–86} Some merocyanine dyes (e.g. dye **48** in Table 1^{50,197}) even show an inverted solvatochromism, i.e. their long wavelength solvatochromic absorption band exhibits first a bathochromic and then a hypsochromic band shift as the solvent polarity increases. This is due to a solvent-induced change of the electronic ground-state structure from a less dipolar (in nonpolar solvents) to a more dipolar chromophore (in polar solvents) with increasing solvent polarity.¹⁹⁷

The search for quantitative relationships between the solvent influence on UV/vis/near-IR spectra and physical solvent parameters led Kundt, in 1878, to propose the rule, later named after him, that increasing dispersion (i.e. increasing index of refraction) of the solvent results in bathochromic shifts of the solute absorption band.⁶⁶ Since then, numerous quantitative relationships between solute light absorption and physical solvent properties, based on different models for solute/solvent interactions (such as, for example, the Onsager reaction field approach) have been established. The discussion of these relationships is outside the scope of this review, and the reader is referred to a selection of publications dealing with various theoretical treatments of solvent effects on electronic spectra.^{74,75,78,79,87–102}

The complexity of intermolecular solute/solvent interactions has led to correspondingly complex, theoretically derived relationships between solvent-induced band shifts and physical parameters of solute and solvent, which, in general practice, have been rather seldom used by chemists in their efforts to quantify the term "solvent polarity". The main shortcomings of the theoretical treatments of solvent effects on electronic spectra are the unavoidable use of simplified model concepts, without due regard to the specific solute/solvent interactions such as hydrogen-bonding, EPD/EPA, and solvophobic interactions. The lack of reliable theoretical calculations of solvent effects in the past, and the inadequacy of defining "solvent polarity" in terms of simple physical solvent constants, have stimulated attempts to introduce empirical scales of solvent polarity, based on convenient, well-known, easily measurable, solvent-sensitive reference processes within the framework of LFE relationships.⁵⁴⁻⁵⁷

B. Solvatochromic Compounds

Because of the simplicity of UV/vis/near-IR spectroscopic measurements, empirical parameters of solvent polarity have been preferably determined by means of solvatochromic compounds. It is assumed that a particular solvent-influenced UV/vis/near-IR absorption is a suitable, representative model for a large class of other solvent-dependent processes. Model processes used to establish spectroscopically empirical scales of solvent polarity have been reviewed.^{1,43,47,54} Solvatochromic compounds suitable as color indicators for solvent polarity measurements have also been reviewed.^{1,103-109} It should be noted that the absorption range of suitable solvatochromic reference compounds does not only include the traditional UV and vis region, but also the near-IR region.¹⁰

In Table 1 solvatochromic compounds, which have been used as UV/vis/near-IR spectroscopic indicators to establish empirical scales of solvent polarity, are compiled. They are roughly ordered according to their solvatochromic range, i.e. their sensitivity to a solvent change. Sometimes, these scales have been given a special name or symbol, after the type of the respective light absorption ($\pi \rightarrow \pi^*$, CT, etc.); this symbol is added in parentheses. Included in Table 1 are also some of those solvatochromic compounds which have been proposed as solvent polarity indicators, for which, however, a complete solvent scale has not been worked out. Naturally, there are many more known solvatochromic compounds than those given in Table 1. It is not easy to draw a distinct line between plain solvatochromic compounds and those which have been occasionally proposed as potential solvent polarity indicators. For a particular solvatochromic compound of Table 1, most of the relevant references dealing with this compound are given, with that reference in which that compound was first proposed as a solvent polarity indicator added in parentheses.

Table 1 contains 35 positively solvatochromic dyes and 35 negatively solvatochromic dyes with 5-(dimethylamino)-5'-nitro-2,2'-bisthiophene (**1**) and 4-(2,4,6-triphenyl-1-pyridinio)-2,6-diphenylphenolate (**36**)

at the respective first places, with regard to their experimentally accessible solvatochromic ranges. In addition, a selection of more recently investigated solvatofluorochromic dyes is included in Table 1, with 1-phenyl-4-[(4-cyano-1-naphthyl)methylene]piperidine (**71**) as the fluorescent compound with the largest measured solvatochromic range. Fluorescent probe molecules have been used not only for the empirical determination of solvent polarities, but also in the study of microheterogeneous media, organized media as well as biochemical and biological systems. Very often, the use of polarity-sensitive probe molecules is the only way to study the structure of binding sites and dynamics of carrier proteins, lipid layers, and natural membranes on a molecular microscopic level. For more examples of fluorescent probe molecules the reader is referred to refs 119a and 261-271.

Most of these fluorescent probes exhibit a positive solvato(fluor)chromism, i.e. a bathochromic shift of the emission band with increasing solvent polarity. A positive solvato(fluor)chromism of the emission band usually corresponds to a positive solvatochromism of the absorption band, as shown by the examples of the merocyanine dyes **5** and **6** in Table 1, the solvent dependence of which has been studied for both their emission and absorption spectrum.¹¹⁹ According to the intramolecular charge transfer on excitation, the first Franck-Condon excited state is much more dipolar than the ground state. Stabilization of this dipolar Franck-Condon excited state, before and after relaxation to the equilibrium excited state, and destabilization of the Franck-Condon ground state relative to the equilibrium ground state, by differential solvation, leads eventually to the observed positive solvato(fluor)chromism. In suitable cases, positively solvatochromic fluorescence bands will be more sensitive to solvent polarity changes than the corresponding absorption bands. Unfortunately, most of the negatively solvatochromic dyes given in Table 1 (e.g. the betaine dyes **36** and **37** and their derivatives) do not exhibit any fluorescence, at least at room temperature.

In the case of the fluorescent polycyclic aromatic hydrocarbons (PAH) such as pyrene **78** in Table 1, instead of the minor solvent-induced shift of their emission bands, the solvent-dependent ratio of emission intensities of two selected vibronic fluorescence bands have been successfully used to set up a solvent polarity scale, called the Pyrene or Py scale.²⁵⁸⁻²⁶⁰

V. Empirical Parameters of Solvent Polarity from UV/Vis/Near-IR Spectroscopic Measurements

A. Single Parameter Approaches

From the total of 78 solvatochromic and solvatofluorochromic compounds in Table 1, which have been proposed and used as potential empirical solvent polarity indicators, up to now only ca. 18 of them have been really used to establish definite, UV/vis/near-IR spectroscopically derived scales of solvent polarity: the Z scale of Kosower,⁵¹ the χ_R and χ_B scale of Brooker et al.,¹¹² the RPM scale (from German "Relatives Polaritätsmass") of Dähne et al.,^{118b} the E_{LMCT} scale of Armand et al.,¹²⁶ the π^* scale of Kamlet,

Table 1. Compilation of Positively and Negatively Solvatochromic as Well as Some Fluorescent Compounds Proposed as UV/Vis/Near-IR Spectroscopic Solvent Polarity Indicators, together with Their Solvatochromic Range, $\Delta\bar{\nu}^a$

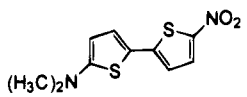
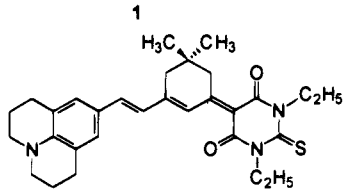
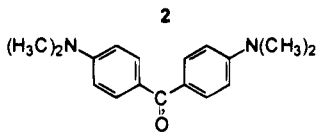
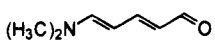
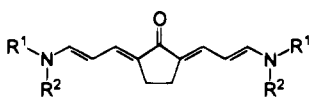
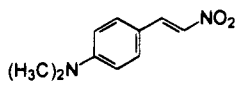
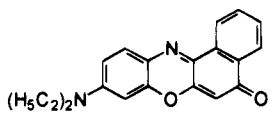
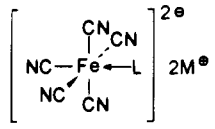
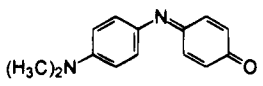
formula formula number	$\Delta\bar{\nu}$ (in cm^{-1}) = $\bar{\nu}$ (nonpolar solvent) - $\bar{\nu}$ (polar solvent)	absorption type ^b (symbol)	ref(s)
(a) Positively Solvatochromic Compounds			
	+4710 = 21460 (C_6H_{14}) - 16750 ($\text{HCONH}_2/\text{H}_2\text{O}$)	$\pi \rightarrow \pi^*$ (-)	111 (111a)
1 	+4400 = 17790 (<i>i</i> - C_8H_{18}) - 13390 (lutidine/ H_2O)	$\pi \rightarrow \pi^*$ (χ_R scale)	112-114 (112)
2 	+4240 = 30000 (C_6H_{14}) - 25760 ($\text{CF}_3\text{CH}_2\text{OH}$)	$\pi \rightarrow \pi^*$ (-)	115-117 (116)
3 (Michler's Ketone) 	+4030 = 30170 (C_6H_{14}) - 26140 (H_2O)	$\pi \rightarrow \pi^*$ (RPM scale)	118 (118b)
4 	+4010 = 22120 (toluene) - 18110 (H_2O) (for 5)	$\pi \rightarrow \pi^*$ (-)	119 (119b)
5 ($\text{R}^1 = \text{CH}_3$; $\text{R}^2 = \text{C}_6\text{H}_5$) 6 ($\text{R}^1 = \text{CH}_2\text{CO}_2\text{Na}$; $\text{R}^2 = \text{C}_6\text{H}_5$) 	+4000 = 25640 (C_6H_{12}) - 21640 (CH_2I_2)	$\pi \rightarrow \pi^*$ (-)	120, 121 (121)
7 	+3780 = 20640 (C_6H_{14}) - 16860 (H_2O)	$\pi \rightarrow \pi^*$ (-)	114, 122, 123 (123)
8 (Nile Red)  $\text{M}_2[\text{Fe}^{\text{III}}(\text{CN})_5 \text{L}]$	+3420 = 23420 (prop.carb.) - 20000 (H_2O) (for 9)	LMCT (E_{LMCT} scale)	124-126 (126)
9 ($\text{L} = \text{---N---NH}$; $\text{M} = \text{Na}$)			
10 ($\text{L} = \text{---N---NMe}_2$; $\text{M} = \text{Na}$)			
11 ($\text{L} = \text{---N---NH---(CH}_2\text{)}_{17}\text{---CH}_3$) ($\text{M} = \text{H}_3\text{C---(CH}_2\text{)}_{15}\text{---NMe}_3$) 	+2970 = 18120 (<i>c</i> - C_6H_{12}) - 15150 ($\text{CF}_3\text{CH}_2\text{OH}$)	$\pi \rightarrow \pi^*$ (-)	114, 127-132 (131a)
12 (Phenol blue)			

Table 1 (Continued)

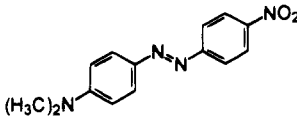
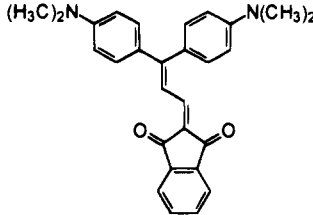
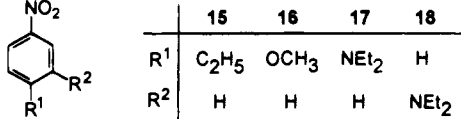
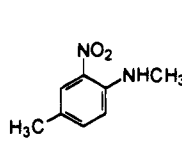
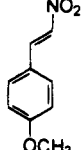
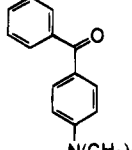
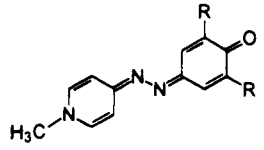
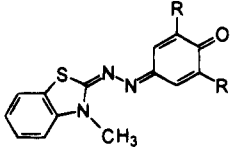
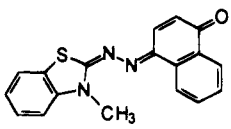
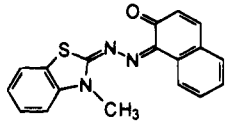
formula formula number	$\Delta\bar{\nu}$ (in cm^{-1}) = $\bar{\nu}$ (nonpolar solvent) - $\bar{\nu}$ (polar solvent)	absorption type ^b (symbol)	ref(s)
(a) Positively Solvatochromic Compounds (Continued)			
	+2700 = 22620 (C_6H_{14}) - 19920 (DMSO)	$\pi \rightarrow \pi^*$ (-)	133-137 (136c)
13			
	+2600 = 18940 (C_6H_{14}) - 16340 (CH_3OH)	$\pi \rightarrow \pi^*$ (-)	138 (138)
14			
	+2400 = 34120 (<i>c</i> - C_6H_{12}) - 31720 (DMSO) (for 16)	$\pi \rightarrow \pi^*$ (π^* scale)	47e, 47j, 53, 139-146 (139a)
15 (R ¹ : C ₂ H ₅ , R ² : H)	16 (R ¹ : OCH ₃ , R ² : H)	17 (R ¹ : NEt ₂ , R ² : H)	18 (R ¹ : H, R ² : NEt ₂)
			
19	20	21	
	+2320 = 20730 (C_6H_{14}) - 18410 (CH_3OH) (for 22)	$\pi \rightarrow \pi^*$ (π_{azo}^* scale)	47h, 94b, 130, 147 (147a)
22 (R = H)	23 (R = C_6H_5)		
			
24 (R = H)	25 (R = C_6H_5)		
			
26			
			
27			

Table 1 (Continued)

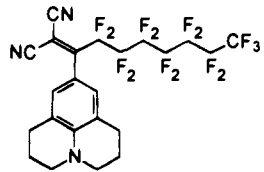
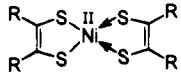
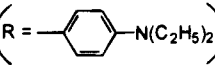
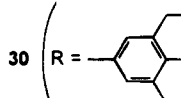
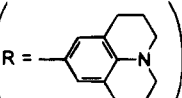
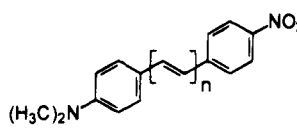
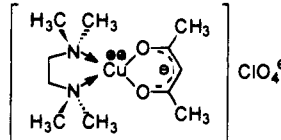
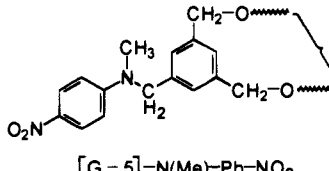
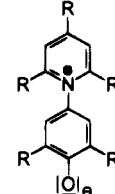
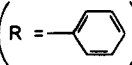
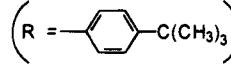
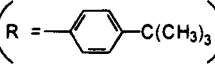
formula formula number	$\Delta\bar{\nu}$ (in cm^{-1}) = $\bar{\nu}$ (nonpolar solvent) - $\bar{\nu}$ (polar solvent)	absorption type ^b (symbol)	ref(s)
(a) Positively Solvatochromic Compounds (Continued)			
 28	+2090 = 19810 (C_5H_{12}) - 17720 ($\text{F}_3\text{C-CHOH-CF}_3$)	$\pi \rightarrow \pi^*$ (P_s scale)	248, 249 (248)
 29 (R = )	+2010 = 9190 (C_7H_{14}) - 7180 (sulfolane) (for 30)	LMCT (E_{Ni} scale)	148 (148)
 30 (R = )			
 31 (n = 1) 32 (n = 2) 33 (n = 3)	+1890 = 23920 (C_7H_{16}) - 22030 (DMSO) (for 31)	$\pi \rightarrow \pi^*$ (-)	149-151 (150)
 34	+1500 = 18420 ($\text{ClCH}_2\text{CH}_2\text{Cl}$) - 16920 (H_2O)	$d \rightarrow d$ of Cu^{II}	103, 105, 107, 152-156 (152a,d)
 35	+1440 = 26250 (CCl_4) - 24810 (DMSO)	$\pi \rightarrow \pi^*$ (π^* scale; cf. 15-21)	157 (157)
(b) Negatively Solvatochromic Compounds			
 36 (R = )	-9730 = 12350 [$(\text{H}_5\text{C}_6)_2\text{O}$] - 22080 (H_2O) (for 36)	$\pi \rightarrow \pi^*$ (with ICT) [$E_{\text{T}}(30)$ or E_{T}^{N} scale]	solvents: 47a-d, 47j, 54, 77b, 94b, 106, 158-173 (36 , 158a; 37 , 160c) polymers: 174-176 chromatography: 80, 161, 177-180
 37 (R = )			

Table 1 (Continued)

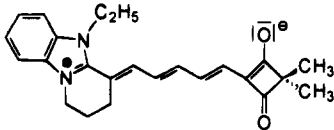
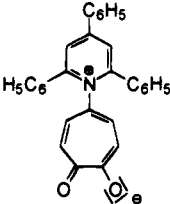
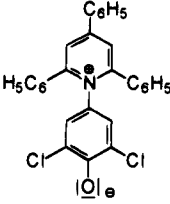
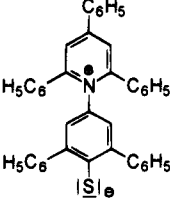
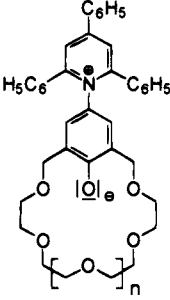
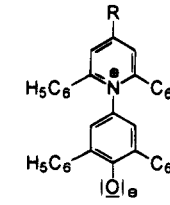
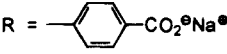
formula formula number	$\Delta\bar{\nu}$ (in cm^{-1}) = $\bar{\nu}$ (nonpolar solvent) - $\bar{\nu}$ (polar solvent)	absorption type ^b (symbol)	ref(s)
(b) Negatively Solvatochromic Compounds (Continued)			
 a merocyanine dye 38	-9500 = 14600 (toluene) - 24100 (H_2O)	$\pi \rightarrow \pi^*$ (χ_B scale)	112, 113 (112)
 39	-9310 = 15290 (THF) - 24600 (H_2O)	$\pi \rightarrow \pi^*$ (with ICT)	181 (181)
 40	-8970 = 15480 (THF) - 24450 (H_2O)	$\pi \rightarrow \pi^*$ (with ICT) [$E_T(33)$ scale]	119a, 182 (182)
 41	-8780 = 11920 (thiophene) - 20700 (glycol)	$\pi \rightarrow \pi^*$ (with ICT) [$E_T^S(30)$ scale]	183 (183)
 42 ($n=0$) 43 ($n=1$) 44 ($n=2$)	-8120 = 14970 (CHCl_3) - 23090 (H_2O) (for 43)	$\pi \rightarrow \pi^*$ (with ICT)	184 (184)
 45	-7810 = 13590 (EtOAc) - 21400 (H_2O)	$\pi \rightarrow \pi^*$ (with ICT)	185 (185)
R = 			

Table 1 (Continued)

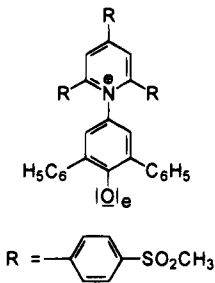
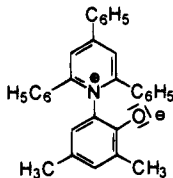
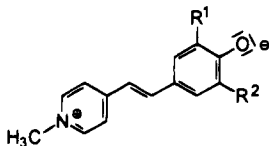
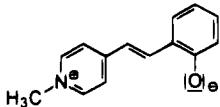
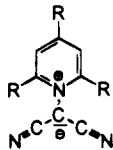
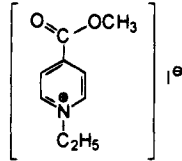
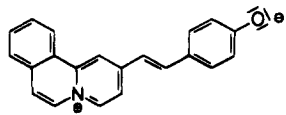
formula formula number	$\Delta\bar{\nu}$ (in cm^{-1}) = $\bar{\nu}$ (nonpolar solvent) - $\bar{\nu}$ (polar solvent)	absorption type ^b (symbol)	ref(s)
(b) Negatively Solvatochromic Compounds (Continued)			
 <p style="text-align: center;">46</p>	<p style="text-align: center;">-7510 = 12410 (<i>o</i>-C₆H₄Cl₂) - 19650 (H₂O)</p>	<p style="text-align: center;">$\pi \rightarrow \pi^*$ (with ICT)</p>	<p style="text-align: center;">186 (186)</p>
 <p style="text-align: center;">47</p>	<p style="text-align: center;">-7290 = 13990 (C₆H₆) - 21280 (H₂O/EtOH)</p>	<p style="text-align: center;">$\pi \rightarrow \pi^*$ (with ICT)</p>	<p style="text-align: center;">187 (187)</p>
 <p style="text-align: center;">a stilbazolium dye</p> <p style="text-align: center;">48 (R¹ = R² = H) 49 (R¹ = H, R² = CMe₃) 50 (R¹ = R² = CMe₃)</p>	<p style="text-align: center;">-6490 = 16130 (CHCl₃) - 22620 (H₂O) (for 48)</p>	<p style="text-align: center;">$\pi \rightarrow \pi^*$</p>	<p style="text-align: center;">solvents: 50, 100, 130, 188-200 (50) polymers: 201</p>
 <p style="text-align: center;">a stilbazolium dye</p> <p style="text-align: center;">51</p>	<p style="text-align: center;">-6090 = 16080 (CHCl₃) - 22170 (H₂O)</p>	<p style="text-align: center;">$\pi \rightarrow \pi^*$</p>	<p style="text-align: center;">202</p>
 <p style="text-align: center;">52</p>	<p style="text-align: center;">-6390 = 14660 (CHCl₃) - 21050 (H₂O/CH₃OH)</p>	<p style="text-align: center;">$\pi \rightarrow \pi^*$</p>	<p style="text-align: center;">203</p>
 <p style="text-align: center;">53</p>	<p style="text-align: center;">-5960 = 23270 (C₅H₅N) - 29230 (CH₃OH)</p>	<p style="text-align: center;">CT, intermolecular (Z scale)</p>	<p style="text-align: center;">3, 44, 51, 170, 194, 204-210 (51)</p>
 <p style="text-align: center;">a stilbazolium dye</p> <p style="text-align: center;">54</p>	<p style="text-align: center;">-5590 = 15600 (H₃CCOCH₃) - 21190 (H₂O)</p>	<p style="text-align: center;">$\pi \rightarrow \pi^*$</p>	<p style="text-align: center;">211 (211)</p>

Table 1 (Continued)

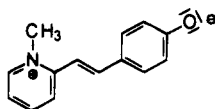
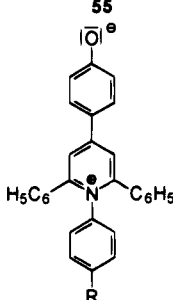
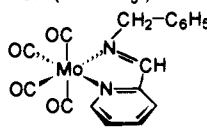
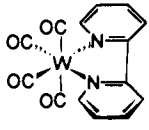
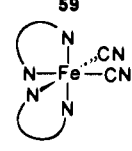
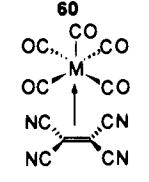
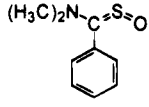
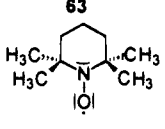
formula formula number	$\Delta\bar{\nu}$ (in cm^{-1}) = $\bar{\nu}$ (nonpolar solvent) - $\bar{\nu}$ (polar solvent)	absorption type ^b (symbol)	ref(s)
(b) Negatively Solvatochromic Compounds (Continued)			
 a stilbazolium dye	-5350 = 18120 ($\text{ClCH}_2\text{CH}_2\text{Cl}$) - 23470 (H_2O)	$\pi \rightarrow \pi^*$	195b, 212
 55 56 (R = OCH_3) 57 (R = CH_3)	-4370 = 19550 ($\text{ClCH}_2\text{CH}_2\text{Cl}$) - 23920 ($\text{CF}_3\text{CH}_2\text{OH}$) (for 56)	$\pi \rightarrow \pi^*$	174, 213 (213)
 $\text{Mo}^0(\text{CO})_4(\text{diimine})$	-3880 = 17120 (C_6H_{14}) - 21000 (HCONH_2)	MLCT (E_K scale)	125, 214 (214)
 $\text{W}^0(\text{CO})_4(\text{bipy})$	-3680 = 17425 (<i>i</i> - C_6H_{18}) - 21105 (CH_3OH)	MLCT (E_{MLCT}^* scale)	125, 215-219 (216)
 $\text{Fe}^{\text{II}}(\text{phen})_2(\text{CN})_2$ (phen = 1,10-phenanthroline)	-3380 = 16000 (H_3CCOCH_3) - 19380 (H_2O)	MLCT	103, 107, 116, 125, 153, 154, 156, 173, 215a, 220-224 (103, 156, 221c)
 $(\eta^2\text{-TCNE})\text{M}(\text{CO})_5$ 61 (M = W) 62 (M = Cr)	-3000 = 12360 (CHCl_3) - 15360 (glyme) (for 61)	MLCT [$E_{\text{CT}}(\pi)$ scale]	125, 225 (225)
	-2650 = 27930 (CCl_4) - 30580 (H_2O)	$n \rightarrow \pi^*$ (E_T^{SO} scale)	226 (226)
 63 64	-2600 = 20960 (C_6H_{14}) - 23560 (H_2O)	$n \rightarrow \pi^*$ (E_B^{N} scale)	227, 228 (228)

Table 1 (Continued)

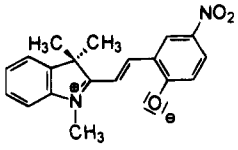
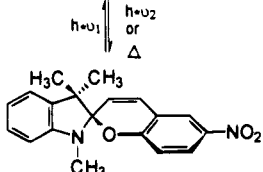
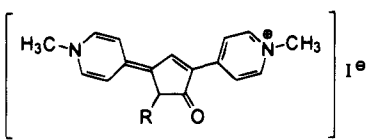
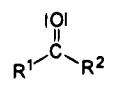
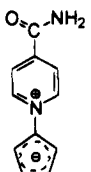
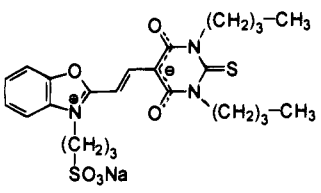

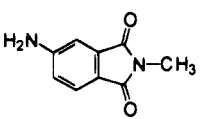
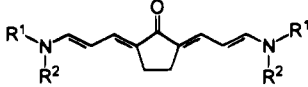
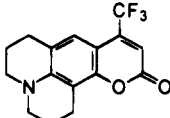
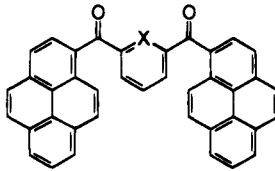
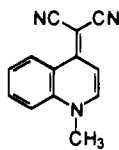
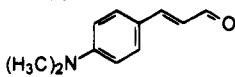
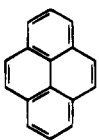
formula formula number	$\Delta\bar{\nu}$ (in cm^{-1}) = $\bar{\nu}$ (nonpolar solvent) - $\bar{\nu}$ (polar solvent)	absorption type ^b (symbol)	ref(s)
(b) Negatively Solvatochromic Compounds (Continued)			
 65a $\lambda_{\text{max}} = 538 \text{ nm}$ (EtOH)	-2010 = 16580 (toluene) - 18590 ($\text{C}_2\text{H}_5\text{OH}$) (for 65a)	$\pi \rightarrow \pi^*$	201b, 229-237 (232)
 65b $\lambda_{\text{max}} = 330 \text{ nm}$ (EtOH)			
 66 (R = CH_3) 67 (R = C_6H_5)	-2010 = 17040 (C_6H_{14}) - 19050 (H_2O) (for 67)	$\pi \rightarrow \pi^*$	238 (238)
 68 R ¹ , R ² = alkyl	-1865 = 35870 (CCl_4) - 37735 ($\text{CF}_3\text{CH}_2\text{OH}$) (for acetone)	$n \rightarrow \pi^*$ (Φ scale)	239 (239b)
 69	-1480 = 17790 (C_6H_6) - 19270 (H_2O)	$\pi \rightarrow \pi^*$ (enzochromism)	159b, 240, 241 (241)
 Merocyanine 540 (MC-540)	-1180 = 17420 ($\text{C}_6\text{H}_6/\text{CH}_3\text{OH}$) - 18600 (H_2O)	$\pi \rightarrow \pi^*$	242-247 (242)
(c) Some Solvatofluorochromic Compounds ^c			
 a „fluoroprobe” dye	+10200 = 24600 (C_6H_{14}) - 14400 (CH_3CN)	$\pi^* \rightarrow \pi$ (with ICT)	30, 250 (30)
 72	+7900 = 24400 (C_6H_{14}) - 16500 (H_2O)	$\pi^* \rightarrow \pi$ (S scale)	251, 252 (251a)

Table 1 (Continued)

formula formula number	$\Delta\bar{\nu}$ (in cm^{-1}) = $\bar{\nu}$ (nonpolar solvent) - $\bar{\nu}$ (polar solvent)	absorption type ^b (symbol)	ref(s)
(c) Some Solvatofluorochromic Compounds ^c (Continued)			
 5 ($R^1 = \text{CH}_3$; $R^2 = \text{C}_6\text{H}_5$) 6 ($R^1 = \text{CH}_2\text{CO}_2\text{Na}$; $R^2 = \text{C}_6\text{H}_5$)	+3980 = 20370 (toluene) - 16390 (H_2O) (for 5)	$\pi^* \rightarrow \pi$ (with ICT)	119, 253 (119b)
 a coumarin laser dye	+3770 = 21980 (<i>c</i> - C_6H_{12}) - 18210 (H_2O)	$\pi^* \rightarrow \pi$ (with ICT)	254
 74 ($X = \text{CH}$: DPB) 75 ($X = \text{N}$: DPP)	+3650 = 21190 (<i>c</i> - C_6H_{12}) - 17540 (CH_3CN) (for 75)	$\pi^* \rightarrow \pi$ (with ICT)	255 (255)
 76	ca. +3000 = ca. 20000 (<i>c</i> - C_6H_{12}) - ca. 17000 (CH_3CN)	$\pi^* \rightarrow \pi$ (with ICT)	256 (256)
 77	+800 = 23530 (C_6H_{12}) - 22730 (H_2O)	$\pi^* \rightarrow \pi$ (with ICT)	257 (257)
 78 (Pyrene = Py) and other polycyclic aromatic hydrocarbons (PAH) as well as aromatic nitrogen hydrocarbons (PANH) such as benzo[ghi]perylene (BPe), benzo[e]pyrene (BePy), and coronene (Cor)	solvent-dependent ratios of emission intensities of selected vibronic fluorescence bands of pyrene (I_1/I_3) and other PAH's and PANH's	$\pi^* \rightarrow \pi$ (Py scale)	258-260 (259)

^a $\Delta\bar{\nu}$ is equal to the difference in wavenumbers of their long-wavelength absorption (or emission) maxima as measured in two solvents of maximum difference in solvent polarity. Within the three groups, the solvatochromic compounds are roughly ordered to their decreasing solvatochromic range. ^b CT = charge-transfer absorption. ICT = intramolecular charge-transfer. LMCT (or $\pi \rightarrow d$) = ligand-to-metal charge-transfer absorption. MLCT (or $d \rightarrow \pi^*$) = metal-to-ligand charge-transfer absorption. ^c Compounds with solvent-dependent position of the emission band in their fluorescence spectrum; $\Delta\bar{\nu}$ corresponds to the difference in wavenumbers of the emission bands as measured in two solvents of maximum difference in solvent polarity.

Abboud, and Taft (KAT),^{139a} the π_{220}^* scale of Buncel et al.,^{147a} the E_{NI} scale of Freyer,¹⁴⁸ the P_s scale (from spectral polarity index) of Middleton et al.,²⁴⁸ the $E_{\text{T}}(30)$ scale of Dimroth and Reichardt,^{158a} the E_{K} scale of Walther,²¹⁴ the E_{MLCT}^* scale of Lees et al.,²¹⁶ the $E_{\text{CT}}(\pi)$ scale of Kaim et al.,²²⁵ the E_{T}^{SO} scale of Walter et al.,²²⁶ the E_{B} scale of Wrona et al.,²²⁸ the ϕ scale of Dubois et al.,^{239b} the S scale of Zelinskii et al.,^{251a} and the Py (or pyrene) scale of Dong and Winnik,²⁵⁹ further developed by Acree et al.²⁶⁰

Most of these scales are based on the spectral data of a single standard probe (or reporter) molecule. They are, therefore, of somewhat limited value in the correlation analysis of other solvent-dependent processes because they respond to a combination of nonspecific and specific solute/solvent interactions, which are typical for the chemical structure of the probe molecule, i.e. its ability to register dispersion, dipole/dipole, hydrogen-bond, and other possible intermolecular interactions. In applying these param-

eters, it is tacitly assumed that the probe/solvent interactions in the reference system used to develop a particular solvent scale are similar to those in that system whose solvent dependence is under study. One cannot expect that a single parameter is universally useful for all kinds of solvent-sensitive processes. On the other hand, correlation analysis with solvent parameters based on a single probe molecule, the probe/solvent interactions of which are well understood and clearly defined (as in some cases given in Table 1), can lead to valuable and significant conclusions about the solvent-dependent process under study. One should remember that the main purpose of solvent polarity scales is, after all, the systematic correlation and analysis of chemical and physicochemical properties in solution.

Although formally single-probe solvent parameters, three of the parameters mentioned in Table 1 are based on more than a single reference compound: the ϕ scale of Dubois et al.,^{239b} the π^* scale of Kamlet, Abboud, and Taft,^{139a} and the π_{azo}^* scale of Buncl et al.^{147a} These parameters are derived by means of averaging processes, using several, chemically closely related solvatochromic probe molecules.

The ϕ scale is based on the position of the solvent-sensitive $n \rightarrow \pi^*$ transition of a selection of saturated aliphatic ketones **68**, measured in *n*-hexane as reference solvent.^{239a}

The π^* scale is based on solvent-induced shifts of the longest wavelength $\pi \rightarrow \pi^*$ absorption band of seven nitroaromatic indicators: 4-ethylnitrobenzene (**15**), 4-methoxynitrobenzene (**16**), 4-(diethylamino)nitrobenzene (**17**), 3-(diethylamino)nitrobenzene (**18**), 2-(methylamino)-5-methylnitrobenzene (**19**), 4-methoxy- β -nitrostyrene (**20**), and 4-(dimethylamino)benzophenone (**21**). This electronic transition is connected with an intramolecular charge transfer from the electron-donor part (OMe, NR₂, alkyl) to the acceptor part (NO₂, COC₆H₅) through the aromatic system. Hence, the first excited state is more dipolar than the ground state, with the observed positive solvatochromism as consequence. The solvent-induced band shifts of these seven nitroaromatics have been employed in the initial construction of the π^* scale, which was then expanded and refined by multiple least-squares correlations with additional solvatochromic indicators. The optimized average π^* values were normalized to give $\pi^* = 0.00$ for cyclohexane and $\pi^* = 1.00$ for dimethyl sulfoxide. The choice of more than just one indicator, whose solvatochromic shifts have been averaged, was aimed at preventing the inclusion of specific probe/solvent effects (e.g. hydrogen bonding) and spectral anomalies (e.g. change of band shape or vibrational fine structure). The π^* values measure dispersive, inductive, and electrostatic probe/solvent interactions and correspond to a blend of polarizability and dipolarity of the solvent. For correlation of solvent-dependent properties with a polarizability/dipolarity blend differing from that of the reference compounds, a variable empirical polarizability parameter δ must be added to π^* .^{139c} This parameter δ is 0.00 for nonhalogenated aliphatic solvents, 0.50 for polyhalogenated aliphatic solvents, and 1.00 for aromatic solvents. For nonaromatic and nonpolyhalogenated

aliphatic solvents, π^* correlates approximately linearly with the permanent dipole moment of the solvent molecules. π^* values have been used in single-parameter correlations, but more often in multiparameter correlations of solvent effects (cf. section V.C). Compilations of π^* values can be found in references.^{47e,139f} For a critical discussion and for possible improvements of the solvatochromic π^* scale, see the reviews of Buncl et al.^{47h} and Laurence^{47j,272,273} (and the references cited therein).

The appropriateness of choosing seven nitroaromatics as primary solvatochromic probe molecules for the establishment of a solvent scale has been questioned.^{47h,47j,272,273} A new procedure for defining π^* values for new solvents, and refining old values, using only 4-methoxynitrobenzene (**16**) as primary and 4-(dimethylamino)nitrobenzene as secondary solvatochromic indicator, has been recently recommended by Laurence et al.^{47j,272,273} and Abboud et al.²⁷³ These new π^* values of solvents S are now simply obtained by applying eq 1,

$$\begin{aligned} \pi^*(S) &= [\bar{\nu}(S) - \bar{\nu}(\text{c-C}_6\text{H}_{12})]/[\bar{\nu}(\text{DMSO}) - \bar{\nu}(\text{c-C}_6\text{H}_{12})] \\ &= [\bar{\nu}(S) - 34120]/2400 \end{aligned} \quad (1)$$

where $\bar{\nu}$ represents the frequencies of the maximum of the solvatochromic absorption band of **16** in various solvents S and in the reference solvents cyclohexane ($\pi^* = 0.00$) and dimethyl sulfoxide ($\pi^* = 1.00$). A collection of such newly defined, revised π^* values for 229 solvents has been given very recently.²⁷³ These new π^* values are directly experimentally available and they are no longer averaged quantities. It has been stated that it is better to study one good model (i.e. one solvatochromic probe molecule) with precision than to take the average of results obtained from several poorer models.^{47j}

Nevertheless, attempts have been made to use the same approach introduced by Kamlet, Abboud, and Taft,¹³⁹ with however, a different set of primary solvatochromic indicators. By means of the six novel, positively solvatochromic azomerocyanine dyes **22–27** as primary indicators (cf. Table 1), a new π_{azo}^* scale of solvent polarity has been recently introduced by Buncl et al.^{47h,147a} This new scale, known for 29 solvents, has been formulated by optimizing UV/vis spectral data of the six dyes **22–27**, with the same normalization condition as used by Kamlet, Abboud, and Taft, i.e. $\pi_{\text{azo}}^* = 0.00$ for cyclohexane and $\pi_{\text{azo}}^* = 1.00$ for dimethyl sulfoxide. The suitability of the azomerocyanines **22–27** as primary indicator solutes has been mainly attributed to the fact that the positions of their absorption bands are in the region 440–590 nm, which is far away from the cutoff points of most solvents—in contrast to the nitroaromatics **15–21**, whose absorption bands are in the UV region and can overlap with the light absorption of the solvents used. As in the case of the nitroaromatic solutes **15–21**, the azomerocyanines are practically not sensitive to type-B hydrogen bonding (i.e. H bonding arising from HBD solute to HBA solvent). They are, however, influenced by type-A hydrogen bonding (i.e. H bonding arising from HBD solvent to HBA solute). A comparison of the π^* scale of Kamlet,

Abbond, and Taft with the π_{azo}^* scale of Buncl shows that π^* and π_{azo}^* values are not equal, but satisfactorily linearly correlated with each other.^{47h,147h} The response of azomerocyanines to the polarizability/dipolarity blend of the solvents is quite similar to that found for the nitroaromatic indicator dyes. In correlation analyses of other solvent-dependent processes, it is found that the π_{azo}^* scale works better than the π^* scale if one considers groups of compounds which are structurally more related to the azomerocyanines (e.g. dyes **2**, **8**, **12**, **13**, and **36**), whereas the π^* scale correlates well with solvent effects dealing with nitroaromatic compounds.^{47h,147}

Experimental data providing the basis for various spectroscopically derived solvent polarity scales (from UV/vis/near-IR, NMR, and ESR measurements), have been recently combined by Drago to give a so-called universal scale of solvent polarity S' .²⁷⁴ Over 300 spectral shifts for 30 probe molecules and 31 solvents have been used to produce this S' scale, which is, however, restricted to only nonspecific solute/solvent interactions. An analogous procedure has been used by Brownstein:²⁷⁵ by combination of many different spectroscopic and reactivity data, an S scale of general solvent polarity was developed. Both scales represent statistical averages derived from a great variety of different solvent-dependent processes, and it is claimed that they are of a more general validity than single-probe-based parameters.²⁷⁴ Because of omitting all systems capable of specific solute/solvent interactions (H bonding, EPD/EPA interactions), the S' scale of Drago is believed to represent a "unified scale of nonspecific solvating ability".²⁷⁴ However, this very recently introduced S' scale has still to stand its acid test.

For most chemists, who have to deal with solvent effects, the voluminous supply of solvatochromic indicators and corresponding solvent polarity scales (as shown in Table 1) may be rather confusing at first sight—and he may leave this business to the specialized physical chemist. But, the introduction of simple single-parameter-based solvent scales is aimed at helping the working chemist in his daily laboratory work to understand qualitatively and to correlate quantitatively the particular solvent effect under study.¹⁻¹⁵ It should be mentioned that many of the empirical parameters of solvent polarity, derived from similar probe molecules, are linearly correlated to each other.⁴⁷ This considerably reduces the difficulties in making the right choice. Normally, one would select that solvent scale, whose underlying reference process is related to the solvent-dependent process under study, and which includes the largest variety of solvents. Surprisingly enough, many of the published solvent scales include, mainly for experimental reasons, only a limited number of solvents which are of interest as reaction media. Today, there are about 300 common solvents available and used, to say nothing of the infinite number of solvent mixtures. A useful solvent scale should at least include representative examples of all different solvent classes, which is not always the case.

Which requirements should be met by a positively or negatively solvatochromic compound for it to be useful for the establishment of a UV/vis/near-IR

spectroscopically derived solvent polarity scale?

(a) First of all, the solvatochromic compound should be easily available, either by a simple synthesis or commercially.

(b) It should be a crystalline compound of definite chemical structure, easy to handle, stable on storage, and particularly stable in solution.

(c) It should possess sufficient solubility in *all* solvents, that is from the least polar (e.g. perfluorohydrocarbons) to the most polar solvents (e.g. water, aqueous electrolyte solutions), in order to get a solvent scale which includes all different types of solvents.

(d) No chemical reaction should occur with the solvent, particularly not with basic or acidic solvents. That is, the chemical nature of the solvent-influenced chromophore should remain unchanged on changing the solvent.

(e) The longest wavelength UV/vis/near-IR absorption band should be shifted bathochromically or hypsochromically with increasing solvent polarity to as large an extent as possible. That is, the light absorption of solvatochromic probe molecules should exhibit maximal sensitivity to changes in the surrounding medium. This behavior is normally found (i) for meropolymethine dyes with a large decrease or increase of the permanent ground-state dipole on excitation by light, i.e. with a large *intramolecular* charge transfer, and (ii) for ground-state ion pairs with annihilation of the opposite charges on excitation by *intermolecular* charge transfer.

(f) The molar decadic extinction coefficient of the solvatochromic absorption band should be sufficiently large, and should not be altered too much by different solvents, in order to allow spectral measurements in highly dilute solutions without solute/solute interactions. That is, spectral measurements must be carried out under conditions without any association or aggregation of the probe molecules. The law of Lambert and Beer should be fulfilled in all solvents in order to make sure that solvent-induced band shifts are not due to association phenomena.

(g) The solvatochromic absorption band should be preferably located within the visible (or near-infrared) region of the electromagnetic spectrum, in order to allow an estimate of solvent polarities visually by eye, and to avoid an overlap of the absorption bands of probe and solvent molecules.

(h) Finally, the chemical structure of the indicator compound should be of the kind that all important nonspecific and specific probe/solvent interactions should be possible. That is, dipole/dipole, dipole/induced dipole, dispersion, hydrogen bonding, EPD/EPA interactions, etc. should be registered by the probe molecule in order to reproduce the overall solvation capability of the solvent, called "solvent polarity". On the other hand, the chemical structure of the probe molecule can be constructed in such a way that it is able to interact with the solvent molecules only in a nonspecific or specific manner. In order to unravel the various solute/solvent interactions, it would be ideal to have to hand probe molecules which interact with solvents by only one interaction mechanism. In this case, the diversity of solute/solvent interactions could be described by

means of multiparameter equations with one solvent parameter for each interaction mechanism (see section V.C for such attempts).

Indeed, some of the indicator molecules of Table 1 are specifically designed for the predominant registration of only one (or two) solute/solvent interactions. For example, the probe molecules of the π^* scale (**15–21**),¹³⁹ π_{azo}^* scale (**22–27**),¹⁴⁷ and P_s scale (**28**)²⁴⁸ register preferably polarizability/dipolarity interactions with the surrounding solvent molecules. Cu(acac)(tmen)ClO₄ (**34**)^{103,152,156} is above all sensitive to solvent Lewis basicity (EPD solvents), whereas Fe(phen)₂(CN)₂ (**61**)^{103,156,221} measures preferably solvent Lewis acidity (HBD solvents). (η^2 -TCNE)M(CO)₅ (**61** and **62** with M = W, Cr)²²⁵ is especially designed to measure the solvent n - and π -donor capability toward planar π -acceptor systems.

A critical evaluation of the various solvent polarity scales, given in Table 1, with respect to points a–h given above, leads to the conclusion that only very few of the respective indicator dyes meet the above-mentioned requirements and are, therefore, of actual practical value. In most cases in Table 1, the relevant solvent parameters are available only for a rather limited number of solvents, mainly because of solubility or stability problems. Among the solvent scales fulfilling with their probe molecules more or less the above-mentioned conditions are the χ_R and χ_B scale of Brooker et al. (dyes **2** and **38**), the π^* scale of Kamlet, Abboud, and Taft (compounds **15–21**) and the improved π^* scale of Laurence and Abboud et al. (compound **16**), as well as the π_{azo}^* scale of Buncel et al. (dyes **22–27**), the $E_T(30)$ scale of Dimroth and Reichardt (dyes **36** and **37**), the E_{LMCT}^* scale of Lees et al. (compound **59**), and the Py scale of Dong, Winnik, and Acree (compound **78** and others). It is difficult to draw a distinct boundary between useful and not so useful solvent polarity scales because some of the more recently introduced scales are certainly likely to be improved by further measurements in more solvents.

As a typical example for a UV/vis/near-IR spectroscopically derived empirical scale of solvent polarity, which includes up to now about 360 solvents, the $E_T(30)$ scale will be outlined in the following chapter.

B. The $E_T(30)$ and E_T^N Scale of Solvent Polarity

$E_T(30)$ values are based on the negatively solvatochromic pyridinium *N*-phenolate betaine dye **36** (cf. Table 1) as probe molecule, and they are simply defined, in analogy to Kosower's *Z* values,⁵¹ as the molar electronic transition energies (E_T) of dissolved **36**, measured in kilocalories per mole (kcal/mol) at room temperature (25 °C) and normal pressure (1 bar),^{158a} according to eq 2. $\tilde{\nu}_{\text{max}}$ is the frequency and

$$\begin{aligned} E_T(30) \text{ (kcal mol}^{-1}\text{)} \\ &= hc\tilde{\nu}_{\text{max}}N_A = (2.8591 \times 10^{-3})\tilde{\nu}_{\text{max}} \text{ (cm}^{-1}\text{)} \\ &= 28591/\lambda_{\text{max}} \text{ (nm)} \end{aligned} \quad (2)$$

λ_{max} the wavelength of the maximum of the longest wavelength, intramolecular charge-transfer $\pi-\pi^*$ absorption band of dye **36**. In the first publication,^{158a}

the betaine dye **36** had, by chance, the formula number **30**. Therefore, the number (30) was added in order to avoid confusion with E_T , often used in photochemistry as abbreviation for triplet energy.

In addition, so-called normalized E_T^N value have been introduced.^{160c} They are defined according to eq 3 as dimensionless figures, using water and tet-

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} = \frac{E_T(\text{solvent}) - 30.7}{32.4} \quad (3)$$

ramethylsilane (TMS) as extreme polar and nonpolar reference solvents, respectively. Hence, the E_T^N scale ranges from 0.000 for TMS, the least polar solvent, to 1.000 for water, the most polar solvent. Prerequisite to the measurement of the polarity of nonpolar solvents was the successful synthesis of a probe with appropriate solubility, i.e. the lipophilic penta-*tert*-butyl-substituted betaine dye **37**, which is, in contrast to **36**, sufficiently soluble for solvatochromic measurements in nonpolar solvents such as aliphatic hydrocarbons and TMS.^{160c} The excellent linear correlation between the E_T values of **36** and **37** for solvents, in which both dyes are soluble, allows the calculation of $E_T(30)$ values according to eq 4 for

$$E_T(30) \text{ (kcal mol}^{-1}\text{)} = \{[28591/\lambda'_{\text{max}} \text{ (nm)}] - 1.808\}/0.9424 \quad (4)$$

nonpolar solvents, in which the primary indicator dye **36** is not soluble enough. In eq 4, λ'_{max} corresponds to the wavelength of the absorption maximum of the secondary indicator dye **37**.^{160c} High $E_T(30)$ or high E_T^N values correspond to high solvent polarity. $E_T(30)$ values (in kcal mol⁻¹ or kJ mol⁻¹) as well as the dimensionless E_T^N values can be equally used. The use of directly determined $E_T(30)$ values in correlations with other energy-based solvent-dependent processes has the advantage of giving immediate insight in the magnitude of the solvent effects observed. For the use in multiparameter correlation equations, the normalized E_T^N values seem to be more suitable.

Both betaine dyes **36** and **37** are rather easy to synthesize;^{158a,160c,161,166,167} betaine dye **36** is commercially available.²⁷⁶ The main step in the synthesis of pyridinium *N*-phenolates, such as **36** and **37**, is the condensation reaction between 2,4,6-triaryl-substituted pyrylium salts with suitably 2,6-disubstituted 4-aminophenols, leading to *N*-(4-hydroxyphenyl)pyridinium salts, which are eventually deprotonated to give the corresponding betaine dyes. Recently, an entirely new synthesis of pyridinium *N*-phenolates, without aryl substituents on the pyridinium ring, has been described:²⁷⁷ thermolysis of quinone diazides such as 2,6-di-*tert*-butyl-4-diazo-2,5-cyclohexadien-1-one in a pyridine/cyclohexane solution affords, via an intermediate carbene, the corresponding 2,6-di-*tert*-butyl-4-(1-pyridinio)phenolate, which exhibits a pronounced negative solvatochromism analogous to dyes **36** and **37**.²⁷⁷ Both dyes, **36** and **37**, are crystalline, stable compounds, stable also in

solution, with one exception: in stronger acidic solvents (e.g. acetic acid), both betaine dyes **36** and **37** are protonated at the oxygen atom of the phenolate part, and the solvatochromic charge-transfer absorption band disappears (reversibly). Addition of traces of an acid to solutions of **36** or **37** immediately changes the color to pale yellow, the color of the protonated forms. The border between acidic and less acidic solvents, for which $E_T(30)$ values are available, is determined by the acidity constant of the corresponding acid of **36**: the pK_a of protonated **36** is 8.65 ± 0.05^{182} or 8.63 ± 0.03^{278} in water. The excellent linear correlation between $E_T(30)$ and Koser's Z values, which are available for acidic solvents (cf. compound **53** in Table 1), allows the calculation of $E_T(30)$ values for such solvents.^{160c} The dichloro-substituted betaine dye **40** is less basic than **36** ($pK_a = 4.78$ for the corresponding acid of **40**) and is a suitable additional indicator molecule for more acidic solvents.¹⁸²

The primary indicator dye **36** is sufficiently soluble in most solvents. It is not soluble in perfluorohydrocarbons and only sparingly soluble in water (solubility of **36** in water ca. 2×10^{-6} mol/L²⁷⁸). In order to obtain probe molecules soluble in perfluorohydrocarbons, the syntheses of perfluor- and trifluoromethyl-substituted as well as hepta-*tert*-butyl- and (1-adamantyl)-substituted derivatives of **36** have been carried out.²⁷⁹ However, these variants of **36** were also not soluble in perfluorohydrocarbons. The solubility in water and aqueous electrolyte solutions was improved by introduction of hydrophilic substituents in **36** to give the more water-soluble betaine dyes **45**¹⁸⁵ and **46**.¹⁸⁶ Again, the linear correlation between the E_T values of **45** and **46** with that of **36** allows the determination of $E_T(30)$ values for aqueous electrolyte solutions.¹⁸⁶

The primary indicator betaine dye **36** exhibits an unusual high solvatochromic band shift: its negatively solvatochromic, intramolecular CT absorption band is hypsochromically shifted by 9730 cm^{-1} (357 nm) on going from diphenyl ether ($\lambda_{\text{max}} = 810 \text{ nm}$) to water ($\lambda_{\text{max}} = 453 \text{ nm}$). Solutions of **36** are red in methanol, violet in ethanol, blue in isoamyl alcohol, green in acetone, and yellowish-green in ethyl acetate, thus covering the whole visible region and allowing even a visual estimate of the solvent polarity. For color photographs of a corresponding test tube experiment see refs 44 and 106b. The complete UV/vis spectrum of **36**, measured in 1,4-dioxane, acetonitrile, and ethanol and its protonated form can be found in ref 280. It should be noted that the IR,^{281a} ¹H NMR,^{165a,281b,282} and ¹³C NMR spectra^{165a} of **36** (and some of its derivatives) have also been measured and analyzed.

The outstanding negative solvatochromism of betaine dye **36** stems from the unequal, differential solvation of its highly dipolar equilibrium ground state and its less dipolar first Franck-Condon excited state with increasing solvent polarity. For a close derivative of **36**, the 2,6-di-*tert*-butyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate, which is soluble enough in 1,4-dioxane for dipole determinations, the permanent dipole moments of the ground state (μ_g) and excited state molecule (μ_e) have been determined

in 1,4-dioxane: $\mu_g = 14.8 \pm 1.2 \text{ D}^{74a,159a}$ and $\mu_e = 6.2 \pm 0.3 \text{ D}^{74a}$. That is, the electronic excitation is connected with a reduction in dipole moment of ca. 9 D, in agreement with a considerable charge transfer from the phenolate to the pyridinium part of the zwitterionic betaine molecule. The position of the intramolecular CT absorption band of **36** depends on the electron affinity of the acceptor part (pyridinium moiety) and the ionization energy of the donor part (phenolate moiety) of the betaine molecule. Therefore, introduction of electron-withdrawing substituents in the acceptor part increases its electron affinity, leading to a bathochromic shift of the CT absorption band of **36**, as experimentally found.⁶³ Ion pairing between the phenolate part of **36** and the cations of added electrolytes, as found in nondissociating solvents, increases the ionization energy of the donor part, leading to a hypsochromic shift of the CT band of **36**.^{160f} Ion pairing with cations of added ionophores is particularly pronounced with the crown ether-substituted betaine dyes **42–44** (cf. Table 1), which exhibit a cation-selective halochromism.¹⁸⁴ Replacement of the phenolate oxygen atom in **36** by sulfur gives the thiobetaine dye **41**, which is accompanied by a bathochromic shift of the CT band due to the reduced ionization energy of Ar-S⁻ as compared to Ar-O⁻.¹⁸³ Altogether, all experimental evidence is in good agreement with an extensive intramolecular charge transfer upon excitation of the primary indicator dye **36**, the main reason for the outstanding negative solvatochromism of **36** and its derivatives **37** and **39–47** (cf. Table 1).

The solvent-mediated stabilization of the highly dipolar, zwitterionic ground state of **36**, relative to its less dipolar excited state, results from the following properties of the betaine molecule: (a) It exhibits a large permanent dipole moment, suitable for the registration of dipole/dipole and dipole/induced dipole interactions. (b) It possesses a large polarizable π -electron system (with 42 π electrons), suitable for the registration of dispersion interactions, which should be somewhat larger with the excited state than with the ground state, because excited states are always more polarizable than the corresponding ground states. And (c) with the phenolate oxygen atom, it has a highly basic EPD center, suitable for interactions with Brønsted acids (through H bonding) and Lewis acids (through EPD/EPA bonding). The positive charge of the pyridinium moiety of **36** is delocalized and sterically shielded, which minimizes the interaction of **36** with EPD solvents. Therefore, the CT absorption of **36** depends also strongly on specific interactions with electrophilic solvents (i.e. HBD and EPA solvents), and only to a much lesser extent on specific interactions with nucleophilic solvents (i.e. EPD solvents).

Altogether, the betaine probe molecule (as well as the other probes of Table 1) measures solute/solvent interactions on a molecular microscopic level, considering solvents as a discontinuum of individual solvent molecules with their own solvent/solvent interactions—in strong contrast to physical parameters such as dielectric constant or refractive index which are macroscopic solvent parameters.

In addition, it should be mentioned that the betaine dye **36** (and its derivatives) does not only exhibit an extraordinary solvatochromism, but that it also shows the phenomena of *thermochromism*, *piezochromism*, genuine *halochromism*,^{160f} and, in case of chirally modified betaine dyes, presumably *chiro-solvatochromism*. These particular, additional properties of pyridinium *N*-phenolate betaine dyes have been reviewed recently.^{106b} Lately, the betaine dye **36** has been proposed as sensitive material in chemical sensors for solvent vapor detection.²⁸³

By taking into account the aforementioned requirements a–h, which should be met by a suitable solvatochromic probe molecule, one can fairly say that the betaine dye **36** (and its derivatives) is certainly a good first choice as an empirical indicator in order to establish a one-parameter solvent scale. Indeed, since its first introduction in 1963,^{158a} the $E_T(30)$ scale has found wide applications in various fields of solvent effects, not only for empirical measurements of the polarity of all kinds of liquid media (solvents, binary solvent mixtures, electrolyte solutions, microheterogeneous solutions, supercritical fluid solvents), but also for the characterization of the polarity of polymers^{174–176} and of chromatographic materials.^{80,161,177–180,112,113}

The unusual spectroscopic behavior of pyridinium *N*-phenolates has led to various additional investigations of the standard betaine dye **36** and its derivatives.

An X-ray analysis of a 4-bromo-substituted derivative of **36**,²⁸⁴ recrystallized from ethanol, shows that all C–C and C–N bonds are of usual length, however, the C–O bond of the phenolate part is, with 129 pm, rather short. The interplanar angle between the pyridinium and phenolate moiety is 65°; the interplanar angles between the five aryl rings and the corresponding two inner rings range from 18° to 70°. That is, the betaine molecule **36** is far from being planar. A hydrogen bond (O–H···O = 271 pm) connects an ethanol molecule to the negatively charged phenolate oxygen atom.²⁸⁴

This hydrogen bonding does not only occur in the crystal lattice; it has also been observed in solution by spectrophotometrical measurements of dilute solutions of **36** in acetonitrile in the presence of increasing amounts of HBD solvents such as alcohols, phenols, and water.¹⁷² Association constants for 1:1 hydrogen-bonded complexes range from $K_{AB} = 2 \text{ M}^{-1}$ for water to $K_{AB} = 6 \times 10^3 \text{ M}^{-1}$ for 3-nitrophenol.¹⁷² Band-shape analysis of the CT absorption band of 2,6-di-*tert*-butyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate in HBD solvents has provided further evidence for such hydrogen bonding.¹⁶⁸ Changes in the shape of the vis spectrum of this betaine dye upon going from dipolar non-HBD solvents to alcohol solvents have been interpreted as evidence for coupling of high-frequency nuclear modes, due to reorganization of the C–N and C–O framework upon excitation, with O–H stretching and bending modes of the solvent.¹⁶⁸ Computer simulation studies (with a molecular modeling program) of the solvation of betaine dye **36** in pure and mixed solvent systems have shown that the preferred docking site for HBD solvents (e.g. water, methanol) is with the C–O[−]

group of the phenolate part of **36**.^{165b,c} Another interesting result of these simulations is the finding that about 40 solvent molecules are necessary to give a fully completed capsule around the betaine molecule **36**.^{165b}

Quantum chemical calculations with dye **36** have been used to test theoretical models for the calculation of the solvent influence on UV/vis spectra,^{94b} and to classify its π system (with intramolecular charge transfer on excitation) in relation to that of polymethine dyes (with charge resonance).^{77b,284} These calculations, which have been carried out with the basic pyridinium *N*-phenolate molecule without any aryl substituents, are in agreement with the observed intramolecular charge-transfer upon excitation by light.^{77b,94b,285}

With betaine dye **36**, dynamic solvent effects on electron transfer (et) reactions in the inverted regime have been studied using ultrafast spectroscopy.¹⁶⁹ That is, the rate of et reactions can be strongly influenced by the dynamics of the corresponding solvent motion. Inverted regime means measurement of nonradiative charge separation of **36** in going from the less dipolar excited state to the highly dipolar ground state, i.e. measurement of the rate of ground-state recovery of a laser-pumped dye solution.¹⁶⁹

Pyridinium *N*-phenolate betaine dyes such as **36** and in particular **47** (cf. Table 1) have been investigated for application in nonlinear optics such as second-harmonic generation (SHG), i.e. frequency doubling of laser radiation.^{187b,286} It was stated that structural features that give rise to strong solvatochromism should also give rise to large second-order molecular polarizabilities (β).^{187b}

Zwitterions such as **36**, particularly 2,6-di-*tert*-butyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate, can be reduced to the corresponding radical anion using alkali metals, and oxidized to the radical cation by Ag(CF₃CO₂) or electrochemically.²⁸⁷ The ESR/ENDOR spectra of solutions in THF indicate predominant spin population either in the pyridinium ring (radical anion), or in the phenolate ring (radical cation). Both redox reactions are reversible and can be used, at least in principle, to construct a molecular battery with pyridinium *N*-phenolate betaine dyes.²⁸⁷

After this short digression into some notable chemical and physical properties of pyridinium *N*-phenolate betaine dyes, which are related to their negative solvatochromism, some further remarks on the $E_T(30)$ scale of solvent polarity shall be finally made.

In Table 2, $E_T(30)$ values (cf. eq 2) and the corresponding dimensionless normalized E_T^N values (cf. eq 3) for about 360 solvents are compiled, based on solvatochromic measurements from various laboratories with the primary and secondary indicator dyes **36** and **37**, respectively.

Some of the $E_T(30)$ values given in Table 2 deviate somewhat from earlier published values. This is due to recently improved methods for purification and drying of the solvents under consideration. Because of the extreme sensitivity of the indicator dye **36** to changes in solvent polarity, traces of polar impurities in less polar solvents can lead to incorrect $E_T(30)$ values, caused by preferential solvation of the betaine

Table 2. Empirical Parameters of Solvent Polarity $E_T(30)$ (Cf. Eq 2) and Normalized E_T^N Values (Cf. Eq 3), Both Derived from the Long Wavelength Vis/Near-IR Absorption Band of the Negatively Solvatochromic Pyridinium *N*-Phenolate Betaine Dyes 36 and 37, for 362 Solvents (Measured at 25 °C and 1 bar)

no.	solvent	$E_T(30)^{a,b}$ (kcal mol ⁻¹)	E_T^N ^c	no.	solvent	$E_T(30)^{a,b}$ (kcal mol ⁻¹)	E_T^N ^c
0	gas phase	(27.1) ^{d,f}	(-0.111)	1	tetramethylsilane, TMS	(30.7) ^{e,f,g}	0.000
Alkanes, Alkenes, Cycloalkanes, and Cycloalkenes							
2	2-methylbutane	(30.9) ^{e,g}	(0.006)	10	<i>n</i> -decane	(31.0) ^{e,g}	(0.009)
3	<i>n</i> -pentane	(31.0) ^{e,g}	(0.009)	11	<i>n</i> -dodecane	(31.1) ^{e,g}	(0.012)
4	<i>n</i> -hexane	(31.0) ^{e,g}	(0.009)	12	cyclohexane	(30.9) ^{e,g}	(0.006)
5	1-hexene	(32.4) ^{e,m}	(0.052)	13	cyclohexene	(32.2) ^{e,m}	(0.046)
6	1-hexyne	(34.3) ^{e,m}	(0.111)	14	<i>cis</i> -decahydronaphthalene	(31.2) ^{e,g}	(0.015)
7	<i>n</i> -heptane	(31.1) ^{e,g}	(0.012)	15	1,2,3,4-tetrahydronaphthalene	33.5 ^h	0.086
8	<i>n</i> -octane	(31.1) ^{e,g}	(0.012)	16	vinylbenzene, styrene	34.8 ^h	0.127
9	<i>n</i> -nonane	(31.0) ^{e,g}	(0.009)				
Haloalkanes and Haloalkenes							
17	dichloromethane	40.7 ^g	0.309	36	1,1-dichloroethene	37.0 ^f	0.194
18	dibromomethane	39.4 ⁱ	0.269	37	(<i>E</i>)-1,2-dichloroethene	(34.2) ^{e,k}	(0.108)
19	diiodomethane	36.5 ⁱ	0.179	38	(<i>Z</i>)-1,2-dichloroethene	(41.9) ^{e,k}	(0.346)
20	trichloromethane, chloroform	39.1 ^{f,g,j}	0.259	39	trichloroethene	35.9 ^{f,j,k}	0.160
21	deuteriochloroform	39.0 ^{f,j}	0.256	40	tetrachloroethene	(32.1) ^{e,m}	(0.043)
22	tribromomethane, bromoform	37.7 ^f	0.216	41	1-chloropropane	37.4 ^{f,j}	0.207
23	tetrachloromethane	32.4 ^g	0.052	42	1-chloro-3,3,3-trifluoropropane	40.7 ^h	0.309
24	trichlorofluoromethane (20 °C)	(33.3) ^{e,k}	(0.080)	43	1,3-dichloropropane	40.2 ^h	0.293
25	bromotrifluoromethane	(34.8) ^{e,k}	0.126	44	2,2-dichloropropane	37.9 ^k	0.222
26	bromoethane	37.6 ^{f,j}	0.213	45	1,2-dichlorohexafluoropropane	(33.6) ^{e,k}	(0.089)
27	1,1-dichloroethane	39.4 ^{f,j}	0.269	46	1,2-dibromopropane	39.1 ^l	0.259
28	1,2-dichloroethane	41.3 ^k	0.327	47	1,2,3-trichloropropane	40.4 ^k	0.299
29	1,2-dibromoethane	38.3 ^l	0.235	48	hexachloropropene	(32.8) ^{e,k}	(0.065)
30	1,1,1-trichloroethane	36.2 ^{l,j,k}	0.170	49	1,4-dichlorobutane	39.5 ^k	0.272
31	1,1,2-trichloroethane	40.3 ^k	0.296	50	1,2-dichlorohexafluorocyclobutane	(33.3) ^{e,k}	(0.080)
32	1,1,1-trichlorotrifluoroethane	(33.8) ^{e,k}	(0.096)	51	hexachloro-1,3-butadiene	(32.2) ^{e,k}	(0.046)
33	1,1,2-trichlorotrifluoroethane	(33.2) ^{e,k}	(0.077)	52	hexachlorocyclopentadiene	(32.8) ^{e,k}	(0.065)
34	1,1,2,2-tetrachloroethane	39.4 ^k	0.269	53	chlorocyclohexane	36.2 ^h	0.170
35	pentachloroethane	36.4 ^k	0.176	54	1,10-dichlorodecane	(36.6) ^{e,k}	(0.182)
Alkylarenes							
55	benzene	34.3 ^{g,n}	0.111	60	1,2,3,4-tetramethylbenzene	(33.0) ^{e,n}	(0.071)
56	methylbenzene, toluene	33.9 ^{g,n}	0.099	61	ethinylbenzene, phenylacetylene	37.2 ^{g,n}	0.201
57	(trifluoromethyl)benzene	(38.5) ^{e,n}	(0.241)	62	cyclohexylbenzene	34.2 ^f	0.108
58	1,4-dimethylbenzene, <i>p</i> -xylene	33.1 ^{g,n}	0.074	63	1-methylnaphthalene	(35.3) ^{e,n}	(0.142)
59	1,3,5-trimethylbenzene	(32.9) ^{e,n}	(0.068)				
Haloarenes							
64	fluorobenzene	37.0 ⁿ	0.194	73	1,3-dichlorobenzene	36.7 ^{n,o}	0.185
65	1,2-difluorobenzene	39.3 ⁿ	0.265	74	1,2,4-trichlorobenzene	36.2 ⁿ	0.170
66	1,3-difluorobenzene	37.3 ⁿ	0.204	75	bromobenzene	36.6 ⁿ	0.182
67	1,4-difluorobenzene	36.4 ⁿ	0.176	76	1,2-dibromobenzene	37.6 ⁿ	0.213
68	1,3,5-trifluorobenzene	(33.2) ^{e,n}	(0.077)	77	1,3-dibromobenzene	36.5 ⁿ	0.179
69	pentafluorobenzene	(38.4) ^{e,n}	(0.238)	78	2,5-dibromo-1-methylbenzene	(34.7) ^{e,n}	(0.123)
70	hexafluorobenzene	34.2 ⁿ	0.108	79	iodobenzene	36.2 ⁿ	0.170
71	chlorobenzene	36.8 ⁿ	0.188	80	1-chloronaphthalene	37.0 ^f	0.194
72	1,2-dichlorobenzene	38.0 ⁿ	0.225	81	1-iodonaphthalene	36.9 ⁿ	0.191
Pyridines and Other Heteroarenes							
82	azine, pyridine	40.5 ^{g,n}	0.302	89	2-fluoropyridine	42.4 ^{g,n}	0.361
83	2-methylpyridine, 2-picoline	38.3 ^{f,j}	0.235	90	2-chloropyridine	41.9 ^p	0.346
84	4-methylpyridine, 4-picoline	39.5 ^m	0.272	91	3-bromopyridine	39.7 ^{g,n}	0.278
85	3,4-dimethylpyridine	38.9 ^{g,n}	0.253	92	2,6-difluoropyridine	43.3 ⁿ	0.389
86	2,6-dimethylpyridine	36.9 ⁿ	0.191	93	pentafluoropyridine	36.3 ⁿ	0.173
87	2,6-di- <i>tert</i> -butylpyridine	(34.0) ^{e,n}	(0.102)	94	2-cyanopyridine (30 °C)	44.2 ^m	0.417
88	2,4,6-trimethylpyridine	36.4 ⁿ	0.176	95	benzo[<i>b</i>]pyridine, quinoline	39.4 ^{f,j}	0.269
Aliphatic and Cycloaliphatic Monoalcohols							
96	methanol	55.4 ^g	0.762	110	2,2,2-trichloroethanol	54.1 ^m	0.722
97	benzyl alcohol	50.4 ^o	0.608	111	1-propanol	50.7 ^{f,j}	0.617
98	ethanol	51.9 ^{f,j}	0.654	112	2,2,3,3-tetrafluoro-1-propanol	59.4 ^{f,j}	0.886
99	ethanol/water (80:20 cl/l)	53.7 ^{f,j}	0.710	113	3-phenyl-1-propanol	48.5 ^o	0.549
100	(±)-1-phenylethanol	46.7 ^o	0.494	114	2-propen-1-ol, allyl alcohol	51.9 ^f	0.654
101	2-phenylethanol	49.5 ^o	0.580	115	2-propyn-1-ol, propargyl alcohol	55.7 ^m	0.772
102	2-methoxyethanol	52.0 ^{f,j}	0.657	116	2-propanol	48.4 ^g	0.546
103	2-ethoxyethanol	51.0 ^{f,m}	0.627	117	1,1,1,3,3,3-hexafluoro-2-propanol	65.3 ^g	1.068
104	2-(<i>n</i> -butoxy)ethanol	50.0 ^f	0.596	118	(±)-1-methoxy-2-propanol	48.6 ^m	0.552
105	2-mercaptoethanol	53.6 ^h	0.707	119	(±)-1-amino-2-propanol	50.1 ^h	0.599
106	2-aminoethanol	51.8 ^{f,j}	0.651	120	1-butanol	49.7 ^{f,j}	0.586
107	2-cyanoethanol	59.6 ^q	0.892	121	(±)-2-amino-1-butanol	50.2 ^f	0.602
108	2-chloroethanol	55.1 ^q	0.753	122	(±)-2-butanol	47.1 ^{f,j}	0.506
109	2,2,2-trifluoroethanol	59.8 ^g	0.898	123	2-methyl-1-propanol, <i>iso</i> -butyl alcohol	48.6 ^o	0.552

Table 2 (Continued)

no.	solvent	$E_T(30)^{a,b}$ (kcal mol ⁻¹)	E_T^N ^c	no.	solvent	$E_T(30)^{a,b}$ (kcal mol ⁻¹)	E_T^N ^c
Aliphatic and Cycloaliphatic Monoalcohols (Continued)							
124	2-methyl-2-propanol, <i>tert</i> -butyl alcohol (30 °)	43.3 ^f	0.389	136	1-octanol	48.1 ^{f,m,o}	0.537
125	1-pentanol, <i>n</i> -amyl alcohol	49.1 ^{f,o}	0.586	137	1-nonanol	47.8 ^m	0.528
126	(±)-2-pentanol, <i>sec</i> -amyl alcohol	46.5 ^{f,j}	0.488	138	3-ethyl-2,4-dimethyl-3-pentanol	37.9 ^q	0.222
127	3-pentanol	45.7 ^{f,j,q}	0.463	139	1-decanol	47.7 ^{m,o}	0.525
128	(±)-2-methyl-1-butanol	48.0 ^h	0.534	140	1-undecanol	47.6 ^m	0.522
129	3-methyl-1-butanol, <i>iso</i> -amyl alcohol	49.0 ^f	0.565	141	1-dodecanol	47.5 ^{m,o}	0.519
130	2-methyl-2-butanol, <i>tert</i> -pentyl alcohol	41.0 ^{m,q}	0.318	142	cyclopentanol	47.0 ^o	0.503
131	(±)-3-methyl-2-butanol	45.7 ^h	0.463	143	cyclohexanol	47.2 ^{f,o}	0.509
132	1-hexanol	48.8 ^{f,o}	0.559	144	2-(hydroxymethyl)furan, furfuryl alcohol	(50.3) ^{f,r}	(0.605)
133	1-heptanol	48.5 ^o	0.549	145	2-(hydroxymethyl)tetrahydrofuran, tetrahydrofurfuryl alcohol	50.3 ^f	0.605
134	3-ethyl-3-pentanol	38.5 ^q	0.241				
135	2,4-dimethyl-3-pentanol	40.1 ^q	0.290				
Aliphatic Polyalcohols							
146	1,2-ethanediol, glycol	56.3 ^{f,j,t}	0.790	154	1,5-pentanediol	51.9 ^{h,t}	0.654
147	(±)-1,2-propanediol	54.1 ^{s,t}	0.722	155	diethylene glycol	53.8 ^{f,j,t}	0.713
148	1,3-propanediol	54.9 ^t	0.747	156	triethylene glycol	52.8 ^{f,j,t}	0.682
149	1,2,3-propanetriol, glycerol	57.0 ^s	0.812	157	tetraethylene glycol	52.2 ^f	0.664
150	(±)-1,2-butanediol	52.6 ^{h,t}	0.676	158	bis(2-hydroxyethyl)sulfane, 2,2'-thiodiethanol	54.5 ^h	0.735
151	(±)-1,3-butanediol	52.8 ^{h,t}	0.682				
152	1,4-butanediol	53.5 ^{h,t}	0.704	159	tris(2-hydroxyethyl)amine, triethanolamine	55.4 ^u	0.762
153	2,3-butanediol (mixture of <i>meso</i> and <i>rac</i> form)	51.8 ^{h,t}	0.651				
Aromatic Alcohols (Phenols)							
160	hydroxybenzene, phenol	53.4 ^v	0.701	180	2,3,6-trimethylphenol	42.9 ^v	0.376
161	2-methylphenol, <i>o</i> -cresol	51.9 ^v	0.654	181	2,6-di- <i>tert</i> -butyl-4-methylphenol	41.9 ^v	0.346
162	3-methylphenol, <i>m</i> -cresol	52.4 ^v	0.670	182	4-fluorophenol	55.5 ^v	0.765
163	4-methylphenol, <i>p</i> -cresol	53.3 ^v	0.697	183	2-chlorophenol	54.7 ^v	0.741
164	2-ethylphenol	50.2 ^v	0.602	184	4-chlorophenol	54.4 ^v	0.731
165	3-ethylphenol	51.6 ^v	0.645	185	4-bromophenol	52.2 ^v	0.664
166	4-ethylphenol	50.2 ^v	0.602	186	2,6-dichlorophenol	46.3 ^v	0.481
167	2-isopropylphenol	50.4 ^v	0.608	187	4-chloro-3-methylphenol	51.0 ^v	0.626
168	2- <i>tert</i> -butylphenol	49.2 ^v	0.571	188	4-methoxyphenol	45.4 ^v	0.454
169	4- <i>tert</i> -butylphenol	50.4 ^v	0.608	189	2,6-dimethoxyphenol	41.8 ^v	0.343
170	2,3-dimethylphenol, 2,3-xyleneol	45.1 ^v	0.444	190	3,5-dimethoxyphenol	50.8 ^v	0.620
171	2,4-dimethylphenol, 2,4-xyleneol	50.3 ^v	0.605	191	3-acetoxyphenol	53.2 ^v	0.694
172	3,4-dimethylphenol, 3,4-xyleneol	47.2 ^v	0.509	192	2-(methoxycarbonyl)phenol, methyl salicylate	45.4 ^v	0.454
173	3,5-dimethylphenol, 3,5-xyleneol	47.5 ^v	0.518				
174	5-isopropyl-2-methylphenol, carvacrol	48.7 ^v	0.556	193	2-(phenoxy-carbonyl)phenol, phenyl salicylate	41.9 ^v	0.346
175	2-isopropyl-5-methylphenol, thymol	48.4 ^v	0.546				
176	2- <i>tert</i> -butyl-4-methylphenol	46.8 ^v	0.497	194	2-aminophenol	47.2 ^v	0.509
177	2,4-di- <i>tert</i> -butylphenol	46.2 ^v	0.478	195	3-aminophenol	47.1 ^v	0.506
178	2,6-di- <i>tert</i> -butylphenol	41.8 ^v	0.343	196	2-nitrophenol	44.4 ^v	0.423
179	2,3,5-trimethylphenol	45.8 ^v	0.466	197	4-cyanophenol	52.2 ^v	0.664
Aliphatic, Cycloaliphatic, and Aromatic Ethers, Thioethers, and Acetals							
198	diethyl ether	34.5 ^{g,j}	0.117	214	oxole, furan	(36.0) ^{e,n}	0.164
199	bis(2-chloroethyl) ether	41.6 ^k	0.336	215	oxolane, tetrahydrofuran	37.4 ^{f,j}	0.207
200	ethyl vinyl ether	36.2 ^f	0.170	216	(±)-tetrahydro-2-methylfuran	36.5 ^{f,j}	0.179
201	di- <i>n</i> -propyl ether	34.0 ^w	0.102	217	tetrahydro-2,5-dimethylfuran	35.1 ^h	0.136
202	diisopropyl ether	(34.1) ^{e,m}	(0.105)		(mixture of <i>cis/trans</i> isomers)		
203	di- <i>n</i> -butyl ether	(33.0) ^{e,g,j}	(0.071)	218	thiole, thiophene	35.4 ⁿ	0.145
204	<i>tert</i> -butyl methyl ether	34.7 ^m	0.124	219	thiolane, tetrahydrothiophene	36.7 ^h	0.185
205	<i>tert</i> -amyl methyl ether, 2-methoxy-2-methylbutane	(34.4) ^{e,h}	(0.114)	220	1,3-dioxolane	43.1 ^f	0.383
206	dimethoxymethane	35.8 ^f	0.157	221	2-methoxy-1,3-dioxolane	44.5 ^h	0.426
207	diethoxymethane	33.9 ^m	0.099	222	oxane, tetrahydropyran	36.2 ^f	0.170
208	1,2-dimethoxyethane	38.2 ^{f,j}	0.231	223	(±)-tetrahydro-3-methylpyran	35.5 ^h	0.148
209	diethylene glycol dimethyl ether, diglyme	38.6 ^{f,j}	0.244	224	5-acetyl-5-methyl-1,3-dioxane	41.5 ^{f,j}	0.333
210	diethylene glycol diethyl ether	37.5 ^{f,j}	0.210	225	1,4-dioxane	36.0 ^{f,g,j}	0.164
211	triethylene glycol dimethyl ether, triglyme	38.9 ^{f,j}	0.253	226	methoxybenzene, anisole	37.1 ^{j,n}	0.198
212	(±)-methyloxirane, propylene oxide	39.8 ^f	0.281	227	(methylthio)benzene, thioanisole	37.0 ⁿ	0.194
213	(±)-2-(chloromethyl)oxirane, epichlorohydrin	44.5 ^f	0.426	228	ethoxybenzene, phenetole	36.6 ⁿ	0.182
				229	1,2-dimethoxybenzene, veratrole	38.4 ^f	0.238
				230	dibenzyl ether	36.3 ⁿ	0.173
				231	diphenyl ether (30 °C)	35.3 ^{f,j}	0.142
Aliphatic, Cycloaliphatic, and Aromatic Ketones							
232	propanone, acetone	42.2 ^{f,j}	0.355	237	3-methyl-2-butanone, isopropyl methyl ketone	40.9 ^x	0.315
233	1,1,1-trichloroacetone	45.9 ^k	0.469				
234	2-butanone	41.3 ^{f,j}	0.327	238	2-hexanone	40.1 ^x	0.290
235	2-pentanone	41.1 ^x	0.321	239	4-methyl-2-pentanone, isobutyl methyl ketone	39.4 ^{f,j}	0.269
236	3-pentanone	39.3 ^{f,j}	0.265				

Table 2 (Continued)

no.	solvent	$E_T(30)^{a,b}$ (kcal mol ⁻¹)	E_T^N ^c	no.	solvent	$E_T(30)^{a,b}$ (kcal mol ⁻¹)	E_T^N ^c
Aliphatic, Cycloaliphatic, and Aromatic Ketones (Continued)							
240	3,3-dimethyl-2-butanone, <i>tert</i> -butyl methyl ketone	39.0 ^{f*}	0.256	244	2,6-dimethyl-4-heptanone, diisobutyl ketone	38.0 ^{fj}	0.225
241	4-heptanone	38.9 ^y	0.253	245	cyclopentanone	39.4 ^o	0.269
242	2,4-dimethyl-3-pentanone, diisopropyl ketone	38.7 ^{fo}	0.247	246	cyclohexanone	39.8 ^x	0.281
243	5-nonanone, di- <i>n</i> -butyl ketone	37.5 ^w	0.210	247	phenylethanone, acetophenone	40.6 ⁿ	0.306
				248	2,4-pentanedione, acetylacetone	49.2 ^f	0.571
Carboxylic Acids and Anhydrides							
249	formic acid	(54.3) ^{fr}	(0.728)	251	propionic acid	(50.5) ^{fr}	(0.611)
250	acetic acid	(51.7) ^{fr}	(0.648)	252	acetic anhydride	(43.9) ^{frz}	(0.407)
Aliphatic, Cycloaliphatic, and Aromatic Esters							
253	methyl formate	41.9 ^m	0.346	266	dimethyl carbonate	38.2 ^m	0.232
254	ethyl formate	40.9 ^f	0.315	267	diethyl carbonate	36.7 ^o	0.185
255	methyl acetate	38.9 ^m	0.253	268	1,3-dioxolan-2-one, ethylene carbonate (40 °C)	48.6 ^f	0.552
256	methyl trichloroacetate	39.6 ^k	0.275	269	4-methyl-1,3-dioxolan-2-one, propylene carbonate	46.0 ^m	0.472
257	ethyl acetate	38.1 ^{ji}	0.228	270	glycerol triacetate, triacetin	40.4 ^m	0.299
258	ethyl chloroacetate	39.4 ^h	0.269	271	ethyl benzoate	38.1 ^f	0.228
259	ethyl trichloroacetate	38.7 ^h	0.247	272	dimethyl phthalate	40.7 ^f	0.309
260	vinyl acetate	38.0 ^f	0.225	273	di- <i>n</i> -butyl phthalate	39.5 ^h	0.272
261	<i>n</i> -propyl acetate	37.5 ^f	0.210	274	ethyl acetoacetate	49.4 ^f	0.577
262	<i>n</i> -butyl acetate	38.5 ^h	0.241	275	(<i>S</i>)-(-)-ethyl lactate	51.1 ^m	0.630
263	methyl acrylate	38.8 ^h	0.250				
264	methyl methacrylate	37.9 ^h	0.222				
265	4-butyrolactone	44.3 ^f	0.420				
Amides, Thioamides, and Cyanamides							
276	formamide	55.8 ^m	0.775	288	hexahydro-1-methylazepin-2-one, <i>N</i> -methyl- ϵ -caprolactam	41.6 ^h	0.336
277	<i>N</i> -methylformamide	54.1 ^{fi}	0.722	289	<i>N,N</i> -dimethylcyanamide	43.8 ^h	0.404
278	<i>N,N</i> -dimethylformamide, DMF	43.2 ^{fi}	0.386	290	<i>N,N</i> -diethylcyanamide	43.3 ^h	0.389
279	<i>N,N</i> -dimethylthioformamide	44.0 ^h	0.410	291	<i>N,N</i> -diisopropylcyanamide	42.0 ^h	0.349
280	<i>N</i> -methylformanilide	40.8 ^m	0.312	292	1-pyrrolidynecarbonitrile, <i>N</i> -cyanopyrrolidine	42.6 ^h	0.367
281	<i>N</i> -methylacetamide (30 °C)	52.0 ^{fi}	0.657	293	1-piperidynecarbonitrile, <i>N</i> -cyanopiperidine	42.1 ^h	0.352
282	<i>N,N</i> -dimethylacetamide	42.9 ^{fm}	0.377	294	4-morpholynecarbonitrile, <i>N</i> -cyanomorpholine	42.8 ^h	0.373
283	<i>N,N</i> -diethylacetamide	41.4 ^h	0.330				
284	1-methylpyrrolidin-2-one	42.2 ^{fa}	0.355				
285	1-methylpyrrolidin-2-thione	42.8 ^{ha}	0.373				
286	1-ethylpyrrolidin-2-one	41.6 ^m	0.336				
287	1-cyclohexylpyrrolidin-2-one	40.4 ^m	0.299				
Tetra- <i>N</i> -alkyl-Substituted Ureas							
295	1,1,3,3-tetramethylurea	40.9 ^f	0.315	298	hexahydro-1,3-dimethyl-2- oxopyrimidine, dimethyl propylene urea (DMPU)	42.1 ^f	0.352
296	1,1,3,3-tetramethylguanidine	39.3 ^{fi}	0.265				
297	1,3-dimethylimidazolidin-2-one, dimethylethyleneurea (DMEU)	42.5 ^f	0.364				
Aliphatic and Aromatic Nitriles							
299	ethanenitrile, acetonitrile	45.6 ^g	0.460	304	<i>n</i> -butanenitrile, butyronitrile	42.5 ^m	0.364
300	trichloroacetonitrile	40.0 ^h	0.287	305	(cyanomethyl)benzene, phenylacetonitrile	42.7 ^{fi,n}	0.370
301	propanenitrile, propionitrile	43.6 ^{fi}	0.398	306	cyanobenzene, benzonitrile	41.5 ⁿ	0.333
302	3-methoxypropanenitrile	44.4 ^h	0.423				
303	acrylonitrile	46.7 ^f	0.494				
Nitroalkanes and Nitroarenes							
307	nitromethane	46.3 ^{fi}	0.481	309	nitrocyclohexane	39.6 ^m	0.275
308	nitroethane	43.6 ^{fi}	0.398	310	nitrobenzene	41.2 ⁿ	0.324
Aliphatic, Cycloaliphatic, and Aromatic Amines							
311	2-methyl-2-aminopropane, <i>tert</i> -butylamine	(36.5) ^{ef}	(0.179)	317	hexahydropyridine, piperidine	35.5 ^{fi}	0.148
312	1,2-diaminoethane	42.0 ^{fi}	0.349	318	tetrahydro-1,4-oxazine, morpholine	41.0 ^{fi}	0.318
313	diethylamine	35.4 ^{fi}	0.145	319	aminobenzene, aniline	44.3 ^{fi}	0.420
314	triethylamine	(32.1) ^{eg}	(0.043)	320	<i>N</i> -methylaniline	42.5 ^{fi}	0.364
315	tris(<i>n</i> -butyl)amine	(32.1) ^{eg}	(0.043)	321	<i>N,N</i> -dimethylaniline	36.5 ⁿ	0.179
316	azolidine, pyrrolidine	39.1 ^h	0.259				
Phosphorus Compounds (Phosphates)							
322	trimethyl phosphate	43.6 ^y	0.398	327	hexamethylphosphorothioic acid triamide (HMPTS) (30 °C)	39.5 ^h	0.272
323	triethyl phosphate	41.7 ^y	0.324	328	methylphosphonic acid bis(dimethylamide)	42.3 ^f	0.358
324	tri- <i>n</i> -propyl phosphate	40.5 ^y	0.302				
325	tri- <i>n</i> -butyl phosphate	38.9 ^y	0.253				
326	hexamethylphosphoric acid triamide (HMPT)	40.9 ^{fi}	0.315				
Sulfur Compounds (Sulfoxides, Sulfones, Sulfamides)							
329	carbon disulfide	32.8 ^g	0.065	331	methyl (methylthio)methyl sulfoxide	44.0 ^m	0.410
330	dimethyl sulfoxide (DMSO)	45.1 ^{fi,g}	0.444	332	tetrahydrothiophene 1,1-dioxide, sulfolane	44.0 ^{fi}	0.410

Table 2 (Continued)

no.	solvent	$E_T(30)^{a,b}$ (kcal mol ⁻¹)	E_T^N ^c	no.	solvent	$E_T(30)^{a,b}$ (kcal mol ⁻¹)	E_T^N ^c
Sulfur Compounds (Sulfoxides, Sulfones, Sulfamides) (Continued)							
333	(±)-tetrahydro-3-methylthiophene 1,1-dioxide, 3-methylsulfolane	43.0 ^h	0.380	334	<i>N,N,N',N'</i> -tetraethylsulfamide	41.0 ^h	0.318
Selected Liquid Organic Salts ^c							
335	lithium acetate (31%)/sodium acetate (25%)/potassium acetate (44%) eutectic mixture (50–120 °C)	64.7 ^β	1.049	344	<i>n</i> -butylammonium thiocyanate (room temperature)	61.4 ^δ	0.948
				345	<i>sec</i> -butylammonium thiocyanate (room temperature)	61.6 ^δ	0.954
336	dimethylammonium <i>N,N</i> -dimethyl- carbamate, dimcarb	57.2 ^γ	0.818	346	tri- <i>n</i> -butylammonium nitrate (room temperature)	56.7 ^δ	0.803
337	dimethylammonium chloride (130 °C)	60.3 ^β	0.914	347	tetra- <i>n</i> -butylammonium bromide (105–130 °C)	43.3 ^β	0.389
338	ethylammonium chloride (120–150 °C)	62.3 ^β	0.975	348	tetra- <i>n</i> -hexylammonium benzoate (room temperature)	43.9 ^{δ,β}	0.407
339	ethylammonium nitrate (room temperature)	61.6 ^{δ,ε}	0.954	349	tetra- <i>n</i> -butylphosphonium chloride (125–135 °C)	43.0 ^β	0.380
340	<i>n</i> -propylammonium nitrate (room temperature)	60.6 ^δ	0.923	350	tetra- <i>n</i> -butylphosphonium bromide (110–130 °C)	43.5 ^β	0.395
341	di- <i>n</i> -propylammonium thiocyanate (room temperature)	63.3 ^δ	1.006	351	tri- <i>n</i> -butyl- <i>n</i> -dodecylphosphonium chloride (90–130 °C)	42.6 ^β	0.367
342	tetra- <i>n</i> -propylammonium 2-(cyclohexyl- amino)ethanesulfonate (room temperature)	50.9 ^δ	0.623	352	tri- <i>n</i> -butyl- <i>n</i> -dodecylphosphonium bromide (100–130 °C)	44.5 ^β	0.426
343	tetra- <i>n</i> -propylammonium 2-hydroxy-4- morpholinepropanesulfonate (room temperature)	45.5 ^δ	0.457	353	tri- <i>n</i> -butyl- <i>n</i> -dodecylphosphonium iodide (50–75 °C)	42.3 ^β	0.358
Miscellaneous Solvents							
354	carbon dioxide (in its liquid and supercritical state): at 24 °C and 69 bar at 40, 60, and 80 °C and at densities of 0.1–0.9 g/cm ³	(34.5) ^{ε,ζ} (31.1– 31.8) ^η	(0.117) (0.012– 0.034)	358	3-methyl-1,2,3-oxazolium- 5-olate, 3-methylsydnone (40 °C)	49.2 ^m	0.571
355	<i>tert</i> -butylhydroperoxide	49.7 ^θ	0.586	359	3- <i>n</i> -propyl-1,2,3-oxadiazolium- 5-olate, 3- <i>n</i> -propylsydnone	50.1 ^m	0.599
356	isopropylnitrate	43.1 ^f	0.383	360	(±)-(2 <i>S</i> ,3 <i>S</i>)-bis(dimethylamino)- 2,3-dimethoxybutane (DDB)	36.6 ^f	0.182
357	3-methyloxazolidin-2-one	44.9 ^{h,m}	0.438				
Water and Heavy Water							
361	deuterium oxide (99.75 cg/g)	62.8 ^f	0.991	362	water	63.1 ^{f,j}	1.000

^a $E_T(30)$ [kcal mol⁻¹] = 28591/λ_{max} (36) [nm]; cf. eq 2. ^b In the first publication,^{158a} the betaine dye 36 had by chance the formula number 30. Therefore, the number 30 was added in order to avoid confusion with E_T used in photochemistry as the abbreviation for triplet energy. ^c E_T^N = [$E_T(30)$ (solvent) – 30.7]/32.4; cf. eq 3. ^d Because of the low volatility of betaine dye 36, its gas-phase $E_T(30)$ value is not directly measured but calculated; see text and refs 94b, 160c, and 288. ^e The $E_T(30)$ values in parentheses are secondary values, determined by means of the more lipophilic penta-*tert*-butyl-substituted betaine dye 37, and calculated according to $E_T(30)$ [kcal mol⁻¹] = [28591/λ_{max} (37) (nm) – 1.808]/0.9424 (cf. eq 4), which is derived from the correlation equation $E_T(37) = 0.9424E_T(30) + 1.808$ ($n = 16$; $r = 0.9990$; $s = 0.17$); see ref *g* of this table. ^f Reichardt, C.; Harbusch-Görnert, E. *Liebigs Ann. Chem.* **1983**, 721–743. ^g Laurence, C.; Nicolet, P.; Reichardt, C. *Bull. Soc. Chim. Fr.* **1987**, 125–130. ^h Reichardt, C.; Eschner, M.; Schäfer, G. *Liebigs Ann. Chem.* **1990**, 57–61. ⁱ Bekárek, V.; Juřina, J. *Collect. Czech. Chem. Commun.* **1982**, 47, 1060–1068. ^j Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* **1963**, 661, 1–37. Dimroth, K.; Reichardt, C. *Liebigs Ann. Chem.* **1969**, 727, 93–105. Reichardt, C. *Liebigs Ann. Chem.* **1971**, 752, 64–67. ^k Laurence, C.; Nicolet, P.; Lucon, M.; Dalati, T.; Reichardt, C. *J. Chem. Soc., Perkin Trans. 2* **1989**, 873–876. ^l Balakrishnan, S.; Easteal, A. *J. Aust. J. Chem.* **1981**, 34, 933–941. ^m Reichardt, C.; Eschner, M.; Schäfer, G., Unpublished results. Some of the newly measured $E_T(30)$ values deviate somewhat from earlier published values. This is due to better methods of purification of the solvents under consideration. ⁿ Laurence, C.; Nicolet, P.; Lucon, M.; Reichardt, C. *Bull. Soc. Chim. Fr.* **1987**, 1001–1005. ^o Aslam, M. H.; Collier, G.; Shorter, J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1572–1576. ^p Jeblick, W.; Schank, K. *Liebigs Ann. Chem.* **1977**, 1096–1108. ^q Elias, H.; Dreher, M.; Neitzel, S.; Volz, H. *Z. Naturforsch., Part B* **1982**, 37, 684–687. ^r These $E_T(30)$ values in parentheses are secondary values, calculated from Kosower's *Z* values by means of the correlation equation $E_T(30) = 0.752Z - 7.87$ ($n = 15$; $r = 0.998$), established by T. R. Griffiths and D. C. Pugh (*J. Solution Chem.* **1976**, 8, 247–258 and *Coord. Chem. Rev.* **1979**, 29, 129–211) with 15 carefully selected solvents. They can be used in correlations but they are still subject to revision. ^s Kosower, E. M.; Dodiuk, H. *J. Am. Chem. Soc.* **1976**, 98, 924–929. ^t Kosower, E. M.; Dodiuk, H.; Tanizawa, K.; Ottolenghi, M.; Orbach, N. *J. Am. Chem. Soc.* **1975**, 97, 2167–2178. ^u Spange, S.; Keutel, D. *Liebigs Ann. Chem.* **1992**, 423–428. ^v Spange, S.; Lauterbach, M.; Gyra, A.-K.; Reichardt, C. *Liebigs Ann. Chem.* **1991**, 323–329. The $E_T(30)$ values of these phenols have been determined by means of a special technique using solutions of the phenols in 1,2-dichloroethane as inert solvent. ^w Ilić, Z.; Maksimović, Z.; Reichardt, C. *Glasnik Chem. Društva Beograd [Bull. Soc. Chim. Beograd]* **1984**, 49, 17–23. ^x Burden, A. G.; Chapman, N. B.; Duggua, H. F.; Shorter, J. *J. Chem. Soc., Perkin Trans. 2* **1978**, 296–303. ^y Maksimović, Z.; Reichardt, C.; Spirić, A. *Z. Anal. Chem.* **1974**, 270, 100–104. ^z Beaumont, T. G.; Davis, K. M. *J. Chem. Soc., Part B* **1968**, 1010–1014. ^{aa} Mayrhofer, W.; Gritzner, G. *J. Chem. Soc., Faraday Trans. 1990*, 86, 823–828. ^{ab} Harrod, W. B.; Pienta, N. *J. Phys. Org. Chem.* **1990**, 3, 534–544. ^{ac} Schroth, W.; Schädler, H.-D.; Andersch, J. *Z. Chem.* **1989**, 29, 56–57; 129–135. Schroth, W.; Andersch, J.; Schädler, H.-D.; Spitzner, R. *Chemiker-Ztg.* **1989**, 113, 261–271. ^{ad} Poole, S. K.; Shetty, P. H.; Poole, C. F. *Anal. Chim. Acta* **1989**, 218, 241–264. ^{ae} Herfort, I.-M.; Schneider, H. *Liebigs Ann. Chem.* **1991**, 27–31. ^{af} Hyatt, J. A. *J. Org. Chem.* **1984**, 49, 5097–5101. ^{ag} Ikushima, Y.; Saito, N.; Arai, M.; Arai, K. *Bull. Chem. Soc. Jpn.* **1991**, 64, 2224–2229. Ikushima, Y.; Saito, N.; Arai, M. *J. Phys. Chem.* **1992**, 96, 2293–2297. ^{ah} Langhals, H.; Fritz, E.; Mergelsberg, I. *Chem. Ber.* **1980**, 113, 3662–3665. ^{ai} Gonçalves, R. M. C.; Simões, A. M. N.; Albuquerque, L. M. P. C.; Rosés, M.; Ràfols, C.; Bosch, E. *J. Chem. Res. (S)* **1993**, 214–215; *J. Chem. Res. (M)* **1993**, 1380–1388. ^{aj} $E_T(30)$ values for six molten tetraalkylammonium salts have been recently determined indirectly by means of the solvatofluorochromic dye coumarine 153 (Eastman-Kodak): Bart, E.; Meltsin, A.; Huppert, D. *J. Phys. Chem.* **1994**, 98, 3295–3299.

molecule with the more polar component of the solvent mixture.

The $E_T(30)$ scale ranges from 63.1 kcal/mol for water, as the most polar solvent, to 30.7 kcal/mol for tetramethylsilane (TMS), as the least polar solvent. That is, a solvent change from water to TMS reduces the electronic excitation energy of the dissolved indicator dye **36** by 32.4 kcal/mol. In order to avoid the non-SI unit kilocalories per mole (kcal/mol) and the conversion of the $E_T(30)$ values into kilojoules per mole (kJ/mol), in 1983 the normalized E_T^N scale was introduced and defined according to eq 3.^{160c} The dimensionless E_T^N scale ranges now from 1.000 for water to 0.000 for TMS. Normalized E_T^N values are somewhat easier to handle, particularly in multiparameter equations (cf. section V.C). For example, an E_T^N value of 0.503 for cyclopentanol means that this solvent exhibits about 50.3% of the solvent polarity of water, as empirically measured by means of the standard dye **36**. For the definition of the E_T^N scale, it would have been better to use the gas phase as the second standard state. However, because of the low volatility of betaine dye **36**, its gas-phase UV/vis absorption spectrum could not be measured directly. Nevertheless, Table 2 contains a gas-phase $E_T(30)$ value of 27.1 kcal/mol ($E_T^N = -0.111$), which is calculated from linear correlations between measured and calculated λ_{\max} values of **36**. These correlation equations are established either by means of a statistical mechanical line-shape theory [calculated $E_T(30)$ value = 27.1 kcal/mol],²⁸⁸ or by means of a solvation theory derived from a generalized Born model [calculated $E_T(30)$ value = 27.01 ± 1.41 kcal/mol].^{94b} These calculated gas-phase $E_T(30)$ values are in remarkable agreement with another gas-phase $E_T(30)$ value (27.4 kcal/mol), derived from an empirical linear correlation between $E_T(30)$ and ΔG° values of the solvent-dependent equilibrium between configurational isomers of 1,2-dibromo-*tert*-butylcyclohexane.^{160c,289} The calculated gas-phase $E_T(30)$ value of 27.1 kcal/mol, as included in Table 2, corresponds to a wavelength of 1055 nm. That is, in the gas-phase the standard betaine dye **36** should have its long-wavelength absorption maximum in the near-infrared region.

Table 2 includes about 20 different chemical classes of solvents (e.g. alkanes, haloalkanes, arenes, etc.) and allows systematic studies of relationships between $E_T(30)$ values and the chemical constitution of the solvents. According to their E_T values, the organic solvents given in Table 2 can be roughly divided into three large groups: (a) HBD (or "protic") solvents [$E_T(30)$ ca. 47–63 kcal/mol; E_T^N ca. 0.5–1.0], (b) dipolar non-HBD (or "aprotic") solvents [$E_T(30)$ ca. 40–47 kcal/mol; E_T^N ca. 0.3–0.5], and (c) apolar non-HBD solvents [$E_T(30)$ ca. 30–40 kcal/mol; E_T^N ca. 0.0–0.3]. This classification corresponds qualitatively to the famous classification of organic solvents given by Parker in 1962.^{1a,291}

Whereas in non-HBD solvents specific solute **36**/solvent interactions are negligible, they are of importance in HBD solvents. For example, a comparison of the $E_T(30)$ values of methanol (solvent no. 96 in Table 2), 1-butanol (no. 120) and *tert*-butyl alcohol

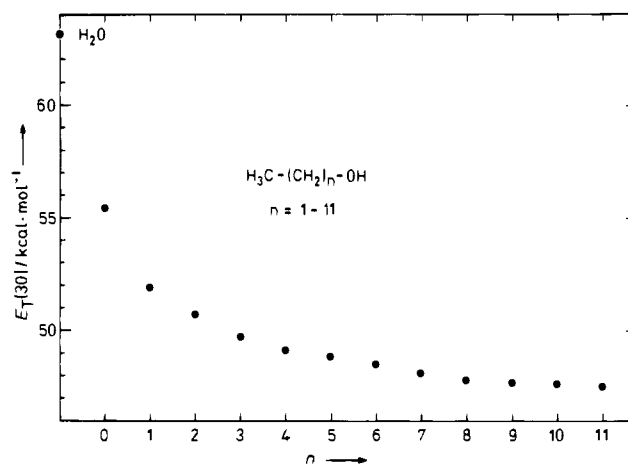


Figure 1. Dependence of the $E_T(30)$ values of homologous 1-alkanols, $H_3C(CH_2)_nOH$, on the chain length n of these alcohols [from $n = 1$ (methanol) to $n = 11$ (1-dodecanol)] with the inclusion of water.

(no. 124) reveals the importance of specific hydrogen-bond interactions between dye **36** and HBD solvents, which are disturbed by steric hindrance of solvation in case of the tertiary alcohol: whereas the $E_T(30)$ value decreases by only 5.7 kcal/mol in going from methanol to 1-butanol, its decrease amounts to 12.1 kcal/mol in going from methanol to *tert*-butyl alcohol. An analogous decrease of the $E_T(30)$ value can be found in going from phenol (no. 160) to 2-*tert*-butylphenol [no. 168; $\Delta E_T(30)$ only 4.2 kcal/mol], and to 2,6-di-*tert*-butylphenol [no. 178; $\Delta E_T(30)$ as large as 11.6 kcal/mol], respectively.

The relation between $E_T(30)$ values and the chain length of a homologous series of solvents is illustrated by the points given in Figure 1 for water and 12 1-alkanols (no. 96, 98, 111, 120, 125, 132, 133, 136, 137, 139, 140, and 141 in Table 2). With increasing chain length of the alcohols, a nonlinear decrease of $E_T(30)$ is observed, which asymptotically reaches a limiting value of about 47 kcal/mol. Obviously, the polarity of a homologous series of solvents can be described in terms of group increments, which are, however, not simply additive, but behave in a logarithmic fashion. It has been shown by Langhals²⁹⁰ that, with respect to their $E_T(30)$ values, this series of homologous 1-alkanols behaves in the same way as a binary mixture of an 1-alkanol with a hydrocarbon. Increasing the alcohol chain length decreases the molar concentration of OH groups in the same way as dilution of an 1-alkanol with a hydrocarbon such as *n*-hexane.²⁹⁰

$E_T(30)$ values have been determined not only for pure solvents, but also for numerous binary solvent/solvent mixtures (Table 3), for many aqueous and nonaqueous electrolyte solutions (Table 4), and for so-called microheterogeneous media such as aqueous and nonaqueous solutions of surfactants, micelles, vesicles, and phospholipid bilayers (Table 5). Because of the diversity of the results obtained, in Tables 3–5 only the systems studied by various research groups are compiled, together with the relevant references in chronological order. This allows the reader to choose quickly the system of interest from the most recent and, because of improved techniques of measurement, more reliable

Table 3. Compilation of References (in Chronological Order) with $E_T(30)$ Values for Binary Solvent/Solvent Mixtures

no.	references	investigated binary mixtures
1	Dimroth, K.; Reichardt, C. <i>Z. Anal. Chem.</i> 1966 , <i>215</i> , 344–350. Reichardt, C. <i>Molecular Interactions</i> ; Ratajczak, H., Orville-Thomas, W., Eds.; Wiley-Interscience: Chichester, 1982; Vol. 3, pp 241–282	mixtures of water with MeOH, EtOH, 2-PrOH, CH ₃ COCH ₃ , pyridine, 2-methylpyridine, 2,6-dimethylpyridine, 1,4-dioxane, and piperidine
2	Maksimović, Z. B.; Reichardt, C.; Spirić, A. Z. <i>Anal. Chem.</i> 1974 , <i>270</i> , 100–104	DMSO/CHCl ₃ ; DMSO/CCl ₄ ; CH ₃ COCH ₃ /CHCl ₃ ; CH ₃ COCH ₃ /CCl ₄ ; CHCl ₃ /CCl ₄ ; (MeO) ₃ PO with CH ₃ COCH ₃ , CHCl ₃ , CCl ₄ , and (<i>n</i> -BuO) ₃ PO; (EtO) ₃ PO with CHCl ₃ and CCl ₄ ; (<i>n</i> -PrO) ₃ PO with CHCl ₃ and CCl ₄ ; (<i>n</i> -BuO) ₃ PO with CHCl ₃ and CCl ₄
3	Krygowski, T. M.; Reichardt, C.; Wrona, P. K.; Wyszomirska, C.; Zielkowska, U. <i>J. Chem. Res. (S)</i> 1983 , 116–117	mixtures of methanol with H ₂ O, HCONH ₂ , propylene carbonate, CH ₃ NO ₂ , CH ₃ CN, DMSO, DMF, CH ₃ COCH ₃ , EtOAc, CHCl ₃ , THF, 1,4-dioxane, Et ₂ O, and C ₆ H ₆
4	Krygowski, T. M.; Wrona, P. K.; Zielkowska, U.; Reichardt, C. <i>Tetrahedron</i> 1985 , <i>41</i> , 4519–4527	mixtures of water with MeOH, EtOH, 1-PrOH, 2-PrOH, CH ₃ CN, DMSO, DMF, CH ₃ COCH ₃ , THF, and 1,4-dioxane
5	Koehler, W.; Froelich, P.; Radechia, R. <i>Z. Phys. Chem. (Leipzig)</i> 1969 , <i>242</i> , 220–224	mixtures of water with CH ₃ COCH ₃ , THF, and 1,4-dioxane
6	Tamura, K.; Ogo, Y.; Imoto, T. <i>Bull. Chem. Soc. Jpn.</i> 1973 , <i>46</i> , 2988–2992	nitrobenzene/benzene
7	Jouanne, J. v.; Palmer, D. A.; Kelm, H. <i>Bull. Chem. Soc. Jpn.</i> 1978 , <i>51</i> , 463–465	H ₂ O/1,4-dioxane, MeOH/CH ₂ Cl ₂
8	Elias, H.; Gumbel, G.; Neitzel, S.; Volz, H. <i>Z. Anal. Chem.</i> 1981 , <i>306</i> , 240–244	mixtures of MeOH with 2-BuOH, <i>t</i> -PeOH, CH ₃ CN, pyridine, and toluene; EtOH/CF ₃ CH ₂ OH
9	Balakrishnan, S.; Easteal, A. J. <i>Aust. J. Chem.</i> 1981 , <i>34</i> , 933–941	EtOH/CH ₃ COCH ₃ , EtOH/CHCl ₃ , CH ₃ COCH ₃ /CH ₂ Cl ₂ , CH ₃ COCH ₃ /CHCl ₃ , Br(CH ₂) ₃ Br/Br(CH ₂) ₂ Br
10	Balakrishnan, S.; Easteal, A. J. <i>Aust. J. Chem.</i> 1981 , <i>34</i> , 943–947	H ₂ O/CH ₃ CN
11	Kosower, E. M.; Kanety, H.; Dodiuk, H.; Striker, G.; Jovin, T.; Boni, H.; Huppert, D. <i>J. Phys. Chem.</i> 1983 , <i>87</i> , 2479–2484	MeOH/1,4-dioxane
12	Koppel, I. A.; Koppel, J. B. <i>Org. React. (USSR) (Engl. Transl.)</i> 1983 , <i>20</i> , 523–546	mixtures of CH ₃ CN and DMSO with H ₂ O, MeOH, EtOH, 2-PrOH, and <i>t</i> -BuOH
13	Koppel, I. A.; Koppel, J. B. <i>Org. React. (USSR) (Engl. Transl.)</i> 1983 , <i>20</i> , 547–560	MeOH/EtOH, EtOH/ <i>t</i> -BuOH, DMSO/CH ₃ CN, pyridine/benzene
14	Nagy, P.; Herzfeld, R. <i>Acta Phys. Chim. Szeged</i> 1985 , <i>31</i> , 735–742; 1987 , <i>33</i> , 53–67	EtOH/CH ₃ COCH ₃ , EtOH/benzene, EtOH/cyclohexane
15	Hicks, J.; Vandersall, M.; Babarogic, Z.; Eisenthal, K. B. <i>Chem. Phys. Lett.</i> 1985 , <i>116</i> , 18–24	C ₃ H ₇ CN/ <i>n</i> -octane, C ₈ H ₁₇ CN/ <i>n</i> -tetradecane
16	Bekárek, V.; Nevěčná, T. <i>Collect. Czech. Chem. Commun.</i> 1985 , <i>50</i> , 1928–1934	CH ₃ COCH ₃ /cyclohexane
17	Nevěčná, T.; Bekárek, V. <i>Collect. Czech. Chem. Commun.</i> 1986 , <i>51</i> , 1942–1947	nitrobenzene/cyclohexane
18	Nevěčná, T.; Vymětalová, J.; Bekárek, V. <i>Collect. Czech. Chem. Commun.</i> 1986 , <i>51</i> , 2071–2076	CH ₃ CN/benzene
19	Mollin, J.; Navrátilová, J.; Bekárek, V. <i>Z. Chem.</i> 1986 , <i>26</i> , 295	H ₂ O/HOCH ₂ CH ₂ OH, H ₂ O/DMSO
20	Engberts, J. B. F. N.; Haak, J. R. <i>Recl. Trav. Chim. Pays-Bas</i> 1986 , <i>105</i> , 307–311	mixtures of water with <i>n</i> -butoxyethanol, <i>t</i> -BuOH, CH ₃ CN, DMSO, and 1,4-dioxane
21	Mooijman, F. R.; Engberts, J. B. F. N. <i>J. Org. Chem.</i> 1989 , <i>54</i> , 3993–3995	H ₂ O/ <i>N</i> -cyclohexylpyrrolidin-2-one
22	Johnson, B. P.; Khaledi, M. G.; Dorsey, J. G. <i>J. Chromatogr.</i> 1987 , <i>384</i> , 221–230. Dorsey, J. G.; Johnson, B. P. <i>Chimica oggi (Milano)</i> 1986 , <i>11</i> , 23–27	H ₂ O/MeOH, H ₂ O/CH ₃ CN
23	Dawber, J. G.; Ward, J.; Williams, R. A. <i>J. Chem. Soc., Faraday Trans. 1</i> 1988 , <i>84</i> , 713–727. Dawber, J. G. <i>J. Chem. Soc., Faraday Trans.</i> 1990 , <i>86</i> , 287–291	mixtures of water with MeOH, EtOH, 1-PrOH, CH ₃ COCH ₃ , and THF; mixtures of CH ₃ COCH ₃ with MeOH, EtOH, 1-PrOH, DMSO, and CHCl ₃ ; mixtures of CHCl ₃ with MeOH, 1-PrOH, and DMSO; MeOH/THF; MeOH/CH ₃ CN; 1-BuOH/CS ₂ ; HCONH ₂ /DMSO
24	Stroka, J.; Herfort, I.-M.; Schneider, H. <i>J. Solution Chem.</i> 1990 , <i>19</i> , 743–753	H ₂ O/ <i>N,N</i> -dimethylpropyleneurea (DMPU)
25	Zalewski, R. I.; Adamczewska, I.; Reichardt, C. <i>J. Chem. Res. (S)</i> 1990 , 280–281; <i>J. Chem. Res. (M)</i> 1990 , 2157–2176	mixtures of water with trimethyl phosphate, triethyl phosphate, and 1,4-dioxane; EtOH/tri- <i>n</i> -butyl phosphate; EtOH/CHCl ₃ ; CH ₃ COCH ₃ /CHCl ₃ (at 30–80 °C)
26	Herfort, I.-M.; Schneider, H. <i>Liebigs Ann. Chem.</i> 1991 , 27–31	mixtures of ethylammonium nitrate (EAN) with H ₂ O, MeOH, <i>t</i> -BuOH, and 1,2-dimethoxyethane; mixtures of DMSO with H ₂ O, EAN, tetraethylammonium nitrate, ethylammonium chloride, and tetraethylammonium chloride
27	Albuquerque, L. M. P.; Ventura, M. C. M.; Moita, M. L. C. <i>J. Chem. Res., Synop.</i> 1992 , <i>3</i> , 92–93	mixtures of H ₂ O with ethane-1,2-diol, propane-1,2-diol, and propane-1,3-diol

Table 3 (Continued)

no.	references	investigated binary mixtures
28	Dutkiewicz, E.; Jakubowska, A.; Dutkiewicz, M. <i>Spectrochim. Acta, Part A</i> 1992 , <i>48</i> , 1409–1414	phenylisothiocyanate/benzene, cyclohexylisothiocyanate/cyclohexane, nitrobenzene/benzene, nitrocyclohexane/cyclohexane
29	Ransdell, R. A.; Wamser, C. C. <i>J. Phys. Chem.</i> 1992 , <i>96</i> , 10572–10575	mixtures of water with DMSO
30	Langhals, H. <i>Angew. Chem.</i> 1982 , <i>94</i> , 739–749; <i>Angew. Chem., Int. Ed. Engl.</i> 1982 , <i>21</i> , 724. Langhals, H. <i>Similarity Models in Organic Chemistry, Biochemistry and Related Fields</i> ; Zalewski, R. I., Krygowski, T. M., Shorter, J., Eds.; Elsevier: Amsterdam, 1991; Chapter 6, pp 283–342	parameters E_D and c^* from the empirical two-parameter equation $E_T(30) = E_D \ln(c_p/c^* + 1) + E_T^*(30)$, describing the polarity of altogether 67 binary solvent mixtures. $E_T(30)$ and $E_T^*(30) =$ empirical solvent polarity parameter of the binary solvent mixture and of its pure, less polar component, respectively; $c_p =$ molar concentration of the pure, more polar component of the binary solvent mixture; E_D and $c^* =$ adjustable parameters specific for the binary solvent mixture under consideration
31	Langhals, H. <i>Tetrahedron Lett.</i> 1986 , <i>27</i> , 339–342. Langhals, H. <i>Z. Phys. Chem. (Leipzig)</i> 1987 , <i>268</i> , 91–96	parameters E_D and c^* of the equation as given before at no. 30 of this table for binary solvent mixtures with limited mutual miscibility
32	Langhals, H. <i>Anal. Lett.</i> 1990 , <i>23</i> , 2243–2258. Langhals, H. <i>GIT Fachz. Lab.</i> 1991 , <i>35</i> , 766–771 [cf. also <i>Aldrichim. Acta</i> 1991 , <i>3</i> , 24; 81; and <i>GIT Fachz. Lab.</i> 1992 , <i>36</i> , 761]	parameters E_D and c^* of the equation as given before at no. 30 of this table for binary mixtures of water with organic solvents, useful for the determination of the water content of water/solvent mixtures
33	Sakong, Y.; Yoo, S.-K.; Lee, I. <i>Bull. Korean Chem. Soc.</i> 1992 , <i>13</i> , 636–642; <i>Chem. Abstr.</i> 1993 , <i>118</i> , 168632m	mixtures of methanol with various organic solvents
34	Bosch, E.; Rosés, M. <i>J. Chem. Soc., Faraday Trans.</i> 1992 , <i>88</i> , 3541–3546. Rosés, M.; Bosch, E. <i>Anal. Chim. Acta</i> 1993 , <i>274</i> , 147–162	preferential solvation coefficients f_2/f_1 from the empirical one-parameter preferential solvation equation $E_T^N = E_{T1}^N + [[x_2(f_2/f_1)(E_{T2}^N - E_{T1}^N)]]/[1 + x_2(f_2/f_1) - 1]]$ describing the polarity of altogether 52 binary solvent mixtures. E_T^N , E_{T1}^N , and $E_{T2}^N =$ normalized empirical solvent polarity parameter of the binary solvent mixture and of its two components, solvent 1 and solvent 2, respectively; $x_2 =$ mole fraction of the more polar solvent 2; $f_2/f_1 =$ proportionality coefficient depending on the tendency of the solvatochromic standard betaine dye to be solvated by the pure solvent 2 in reference to solvent 1 ($f_2 \gg f_1$: strong preferential solvation of the solute by the more polar solvent 2; $f_2 = f_1$: equal solvation of the solute by both solvents 1 and 2)
35	Rosés, M.; Ráfols, C.; Bosch, E. Abstracts 23rd Int. Conference on Solution Chemistry, Leicester, England, August 1993	improvement of the preferential solvation equation for the calculation of E_T^N for binary solvent mixtures as given before at no. 34 of this table. The new equation is based on the simplifying hypothesis that the two solvents mixed, S_1 and S_2 , form as a "third solvent" a 1:1 solvent/solvent interaction complex S_{1-2} . The improved E_T^N equation applies successfully to 65 different binary solvent/solvent mixtures
36	Skwierzynski, R. D.; Connors, K. A. <i>J. Chem. Soc., Perkin Trans. 2</i> 1994 , 467–472	mixtures of water with MeOH, EtOH, 1-PrOH, 2-PrOH, HOCH ₂ CH ₂ OH, DMSO, CH ₃ COCH ₃ , CH ₃ CN, DMF. A one- and a two-parameter equation for the dependence of $E_T(30)$ on x_2 , the mole fraction of the organic cosolvent, is given for altogether 17 binary solvent mixtures
37	Rosés, M.; Ortega, J.; Bosch, E. <i>J. Solution Chem.</i> 1995 , <i>24</i> , in press	alcohol/alcohol mixtures such as MeOH/EtOH, MeOH/HOCH ₂ CH ₂ OH, MeOH/HOCH ₂ CH ₂ OMe, EtOH/HOCH ₂ CH ₂ OH, EtOH/HOCH ₂ CH ₂ OMe, and HOCH ₂ CH ₂ OH/MeOCH ₂ CH ₂ OMe
38	Kipkemboi, P. K.; Easteal, A. J. <i>Aust. J. Chem.</i> 1994 , <i>47</i> , 1771–1781	mixtures of water with <i>t</i> -BuOH and Me ₃ C-NH ₂
39	Drago, R. S.; Hirsch, M. S.; Ferris, D. C.; Chronister, C. W. <i>J. Chem. Soc., Perkin Trans. 2</i> 1994 , 219–230	mixtures of 1,2-dichlorobenzene with MeOH, EtOH, 1-BuOH, <i>t</i> -BuOH, 1-octanol, and CH ₂ Cl ₂

sources. Unfortunately, the results of the various research groups are often not directly comparable because of the use of different ranges and different measures of concentration of one of the two components of the binary systems compiled in Tables 3–5.

The $E_T(30)$ values of binary solvent mixtures (Table 3) are related to their composition, given in volume or mole fraction, not in a simple manner: most binaries behave as more or less nonideal solvent mixtures. A monotonous, but not always linear, change in $E_T(30)$ with mole fraction of one solvent

component is, for example, obtained for some alcohol/water (cf. nos. 1, 3, 4, 23, and 36 in Table 3) and alcohol/alcohol mixtures (nos. 13 and 37). Addition of a small amount of a polar solvent to solutions of dye **36** in nonpolar solvents often causes a disproportionately large hypsochromic band shift because of preferential or selective solvation of the dipolar dye molecule by the more polar component of the binary solvent mixture.^{165,252} Typical examples of solvent mixtures with preferential solvation are 1,4-dioxane/water (nos. 1, 3, 4, 20, and 25) and pyridine/water

Table 4. Compilation of References (in Chronological Order) with $E_T(30)$ Values for Aqueous and Nonaqueous Solutions of Electrolytes (Salts, Ionophores) and Nonelectrolytes (Ionogens)

no.	references	investigated salt solutions
1	Koppel, I. A.; Koppel, J. B. <i>Org. React. (USSR) (Engl. Transl.)</i> 1984 , <i>21</i> , 98–123	(<i>n</i> -Bu ₄ N)Br in H ₂ O; LiCl, NaCl, NaClO ₄ , KBr, (Me ₄ N)Cl, and (<i>n</i> -Bu ₄ N)Br in H ₂ O/MeOH
2	Koppel, I. A.; Koppel, J. B.; Pihl, V. O. <i>Org. React. (USSR) (Engl. Transl.)</i> 1984 , <i>21</i> , 144–159	NaCl, NaClO ₄ , KBr, (Me ₄ N)Cl, (Me ₄ N)ClO ₄ , (Et ₄ N)ClO ₄ , (<i>n</i> -Bu ₄ N)Br, and (<i>n</i> -Bu ₄ N)ClO ₄ in MeOH and DMSO; (<i>n</i> -Bu ₄ N)Br and (<i>n</i> -Bu ₄ N)ClO ₄ in benzene
3	Hollmann, G.; Vögtle, F. <i>Chem. Ber.</i> 1984 , <i>117</i> , 1355–1363 (cf. also, Bock, H.; Herrmann, H.-F. <i>Helv. Chim. Acta</i> 1989 , <i>72</i> , 1171–1185)	excess LiI, NaI, KI, Mg(ClO ₄) ₂ , Ca(SCN) ₂ , and BaI ₂ in acetonitrile
4	Braun, R.; Sauer, J. <i>Chem. Ber.</i> 1986 , <i>119</i> , 1269–1274	LiClO ₄ in MeOCH ₂ CH ₂ OMe, THF, and Et ₂ O (indirect determination)
5	Pocker, Y.; Ciula, J. C. <i>J. Am. Chem. Soc.</i> 1989 , <i>111</i> , 4728–4735	LiClO ₄ in THF and Et ₂ O
6	Harrod, W. B.; Pienta, J. J. <i>Phys. Org. Chem.</i> 1990 , <i>3</i> , 534–544	(<i>n</i> -Bu ₄ P)Br and (<i>n</i> -Bu ₃ P-C ₁₂ H ₂₅)Br in water
7	Herfort, I.-M.; Schneider, H. <i>Liebigs Ann. Chem.</i> 1991 , 27–31	(Et ₄ N)NO ₃ (EAN) in H ₂ O, MeOH, <i>t</i> -BuOH, DMSO, and MeOCH ₂ CH ₂ OMe; (EtNH ₃)Cl, (Et ₄ N)NO ₃ , and (Et ₄ N)Cl in DMSO
8	Reichardt, C.; Schäfer, G.; Milart, P. <i>Collect. Czech. Chem. Commun.</i> 1990 , <i>55</i> , 97–118	LiCl, LiBr, LiI, LiClO ₄ , NaI, KF, KCl, KI, CsI, and Mg(ClO ₄) ₂ in water [c(salt) = 1.0 mol/L]
9	Thompson, P. A.; Simon, J. D. <i>J. Chem. Phys.</i> 1992 , <i>97</i> , 4792–4799	LiClO ₄ , NaClO ₄ , NaI, Mg(ClO ₄) ₂ , and (<i>n</i> -Bu ₄ N)ClO ₄ in acetonitrile [c(salt) = 1.0 mol/L]
10	Reichardt, C.; Asharin-Fard, S.; Schäfer, G. <i>Chem. Ber.</i> 1993 , <i>126</i> , 143–147	LiI, NaI, KI, RbI, CsI, Mg(ClO ₄) ₂ , CaI ₂ , SrI ₂ , BaI ₂ , and (<i>n</i> -Bu ₄ N)I in acetonitrile
11	Desimoni, G.; Faita, G.; Gatti Comini, S.; Righetti, P. P.; Tacconi, G. <i>Tetrahedron</i> 1993 , <i>49</i> , 2093–2100	LiClO ₄ in methanol
12	Rezende, M. C.; Zanette, D.; Zucco, C. <i>Tetrahedron Lett.</i> 1984 , <i>25</i> , 3423–3424. Rezende, M. C.; Dal Sasso, L. I. <i>Rev. Roum. Chim.</i> 1986 , <i>31</i> , 323–326. Rezende, M. C. <i>Tetrahedron</i> 1988 , <i>44</i> , 3513–3522. Lopes de Oliveira, C. C.; Rezende, M. C. <i>J. Braz. Chem. Soc.</i> 1991 , <i>2</i> , 21–24. Gageiro, V.; Aillon, M.; Rezende, M. C. <i>J. Chem. Soc., Faraday Trans.</i> 1992 , <i>88</i> , 201–204	parameters <i>A</i> and <i>c</i> * from the empirical two-parameter equation $E_T(30) = A \ln(c/c^* + 1) + E_T^*(30)$, describing the polarity of at least 20 salt/solvent combinations; $E_T(30)$ and $E_T^*(30)$ = empirical solvent polarity parameters of the salt solution and the pure solvent, respectively; <i>c</i> = molar salt concentration; <i>A</i> and <i>c</i> * = adjustable parameters specific for the salt solution under consideration
13	Spange, S.; Keutel, D. <i>Liebigs Ann. Chem.</i> 1993 , 981–985	urea and <i>N,N'</i> -dimethylurea in water; carbohydrates (glucose, mannose, fructose, saccharose) in water and DMSO
14	Lavallee, R. J.; Zimmt, M. B. <i>J. Phys. Chem.</i> 1994 , <i>98</i> , 4254–4260	(<i>n</i> -Bu ₄ N)PF ₆ and (<i>n</i> -Bu ₃ MeN)PF ₆ in CH ₂ Cl ₂
15	Binder, D. A.; Kreevoy, M. M. <i>J. Phys. Chem.</i> 1994 , <i>98</i> , 10008–10016	LiI in acetonitrile

mixtures (no. 1). In these cases, $E_T(30)$ values do not, in fact, measure the polarity of the bulk solvent mixture, but rather the polarity of the solute-surrounding local solvation shell. Obviously, preferential solvation is induced by the probe molecule and depends on its chemical structure. This implies that solvent polarity parameters obtained in mixtures with a given probe may not be generally valid for the solvation of other probes or solutes dissolved in such solvent mixtures. Whereas in neat solvents all solutes have the same chemical environment and the derived solvent parameters are generally valid, this is not necessarily so for solvent mixtures. A recent careful analysis of the use of chemical probes for the characterization of nonaqueous and aqueous binary solvent mixtures by Marcus has shown^{296c,d} that several chemically dissimilar probes produce convergent values of the respective solvent parameters (at a given composition). That is, preferential solvation need not preclude the practical use of chemical probes in solvent mixtures, particularly for those cases in which probes interact with the components of the binary mixed solvent less strongly as compared to the

mutual self-interaction of the two solvent components.^{296c,d}

Whereas the preferential solvation of ions has been studied extensively,^{1a,7,9} preferential solvation of dipolar solute molecules is less well investigated.^{292–299} Of particular interest are those binary solvent mixtures which exhibit a maximum in the graph describing the dependence of $E_T(30)$ on the composition of the binary solvent mixture. This means that such binary solvent mixtures behave as a more polar medium than either of their two components. Typical examples are trialkyl phosphates/chloroform (no. 2) and DMSO/alcohol mixtures (no. 12). This polarity increase in binary HBA solvent/HBD solvent mixtures has been explained by synergistic effects attributable to specific intermolecular solvent/solvent hydrogen-bond interactions (e.g. P=O⋯HCCl₃, S=O⋯HOR, etc.), which create a new solvent system more polar than the two pure components.^{1a,300} The complex behavior and the $E_T(30)$ and E_T^N values of binary solvent mixtures can be described quantitatively by means of various equations, based on

Table 5. Compilation of References (in Chronological Order) with Applications of Solvatochromic Pyridinium *N*-Phenolate Betaine Dyes (e.g. 36) for the Characterization of Microheterogeneous Media Such as Solutions of Surfactants, Micelles, Vesicles, etc.

no.	references	investigated microheterogeneous media
1	Zachariasse, K. A.; Van Phuc, N.; Kozankiewicz, B. <i>J. Phys. Chem.</i> 1981 , <i>85</i> , 2676–2683	aqueous micellar solutions and some oil-in-water microemulsions of anionic surfactants (sodium decyl, dodecyl, tetradecyl, and hexadecyl sulfate; sodium dodecanoate), cationic surfactants (benzylhexadecyldimethylammonium halides; dodecyl-, tetradecyl-, and hexadecyltrimethylammonium halides), nonionic surfactants (Triton X-100, Brij 35, C ₁₂ EO ₈) as well as multibilayers and sonicated vesicles of dimyristoyl- and dipalmitoylphosphatidylcholine
2	Plieninger, P.; Baumgärtel, H. <i>Ber. Bunsen-Ges. Phys. Chem.</i> 1982 , <i>86</i> , 161–167; <i>Liebigs Ann. Chem.</i> 1983 , 860–875	aqueous micellar solutions of decyl-, dodecyl-, tetradecyl-, hexadecyl-, and octadecyltrimethylammonium bromide; sodium dodecyl sulfate; (dodecyl-dimethylammonium)propane sulfate
3	Drummond, C. J.; Grieser, F.; Healy, T. W. <i>Faraday Discuss. Chem. Soc.</i> 1986 , <i>81</i> , 95–106; <i>Chem. Abstr.</i> 1987 , <i>106</i> , 126332k	aqueous solutions of self-assembled surfactants such as dodecyl- and hexadecyltrimethylammonium halides, dodecyl benzenesulfonate, hexadecylpyridinium bromide, sodium dodecyl sulfate, dodecylethyl(or butyl)dimethylammonium bromide, <i>n</i> -dodecyl octaoxyethylene glycol monoether (C ₁₂ E ₈), dihexadecyl phosphate, L- α -dimyristoyl- and L- α -dipalmitoylphosphatidylcholine
4	Drummond, C. J.; Grieser, F.; Healy, T. W. <i>Chem. Phys. Lett.</i> 1987 , <i>140</i> , 493–498	aqueous micellar solutions of dodecyltrimethylammonium bromide and chloride + electrolytes
5	Kibblewhite, J.; Drummond, C. J.; Grieser, F.; Healy, T. W. <i>J. Phys. Chem.</i> 1987 , <i>91</i> , 4658–4660	micellar solutions of cationic surfactants such as dodecyltrimethylammonium chloride and bromide in 1-pentanol
6	Warr, G. G.; Evans, D. F. <i>Langmuir</i> 1988 , <i>4</i> , 217–224	aqueous micellar solutions of ionic surfactants (dodecyl-, tetradecyl-, and hexadecyltrimethylammonium halides; sodium dodecyl sulfate) and nonionic surfactants [octa(ethylene glycol) mono- <i>n</i> -decyl ether; <i>n</i> -dodecyl β -D-maltoside]
7	Lay, M. B.; Drummond, C. J.; Thistlethwaite, P. J.; Grieser, F. <i>J. Colloid Interface Sci.</i> 1989 , <i>128</i> , 602–604	water-in-oil microemulsions such as sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/hexane/water and didodecyldimethylammonium bromide/tetradecane (or hexane)/water
8	Koppel, I. A.; Koppel, J. B. <i>Org. React. (Tartu)</i> 1989 , <i>26</i> , 78–91; <i>Chem. Abstr.</i> 1990 , <i>113</i> , 230702m	aqueous and some nonaqueous solutions of nonionic surfactants (Triton X-100, Tween-80) and of anionic surfactants (sodium dodecyl sulfate)
9	Kessler, M. A.; Wolfbeis, O. S. <i>Chem. Phys. Lett.</i> 1989 , <i>50</i> , 51–56	aqueous micellar solution of hexadecyltrimethylammonium bromide
10	Zaslavsky, B. Yu.; Miheeva, L. M.; Masimov, E. A.; Djaforov, S. F.; Reichardt, C. <i>J. Chem. Soc., Faraday Trans.</i> 1990 , <i>86</i> , 519–524	aqueous solutions of Dextran-70, poly(ethylene glycol) (PEG 200–20000), and Ficoll-400
11	Handa, T.; Nakagaki, M.; Miyajima, K. <i>J. Colloid Interface Sci.</i> 1990 , <i>137</i> , 253–262	aqueous solutions of micelles (e.g. sodium tetradecyl sulfate) and liposomes
12	Varadaraj, R.; Bock, J.; Valint, P.; Brons, N. <i>Langmuir</i> 1990 , <i>6</i> , 1376–1378	aqueous micellar solutions of ethoxylates, sodium ethoxy sulfates, and sodium sulfates derived from linear and branched hydrocarbon alcohols
13	Varadaraj, R.; Bock, J.; Brons, N.; Pace, S. <i>J. Phys. Chem.</i> 1993 , <i>97</i> , 12991–12994	aqueous solutions of hydrophobically associating water-soluble copolymers of acrylamide and <i>N</i> -alkylacrylamide, forming hydrophobic microdomains by alkyl-chain aggregation; aqueous solutions of anionic and nonionic surfactants (sodium dodecyl sulfate, sodium dodecyl pentaethoxy sulfate, dodecyl pentaethoxylate)
14	Saitoh, I.; Tani, H.; Kamidate, T.; Watanabe, H.; Haraguchi, K.; Abe, S. <i>Anal. Sci.</i> 1993 , <i>9</i> , 345–349	micellar solution (reversed micelles) of <i>N</i> -octanoyl- <i>N</i> -phenylhydroxyamine in tetrachloromethane
15	Hobson, R. A.; Grieser, F.; Healy, T. W. <i>J. Phys. Chem.</i> 1994 , <i>98</i> , 274–278	aqueous micellar solutions of two mixed surfactants: <i>n</i> -dodecyl octaoxyethylene glycol monoether (C ₁₂ E ₈)/sodium dodecyl sulfate (SDS) and C ₁₂ E ₈ / <i>n</i> -dodecyltrimethylammonium chloride (DTAC)

different models for binary solvent mixtures, which are also mentioned in Table 3 (nos. 30–32 and 34–37).

The change in $E_T(30)$ values after addition of an electrolyte (salt or ionophore) to solutions of the probe dye **36** (cf. Table 4) results from a phenomenon called *genuine halochromism*.^{106,184–186} The term *negative (positive) halochromism* was suggested for a hypsochromic (bathochromic) shift of the UV/vis/near-IR absorption band of a dissolved light-absorbing com-

pound on increasing electrolyte concentration, provided this band shift is not caused by a change in the chemical structure of the chromophore.¹⁸⁵ This definition of a genuine halochromism is in contrast to the *trivial halochromism* first described by Baeyer et al.,³⁰¹ studying the salt formation during the reaction of colorless triphenylcarbinol with sulfuric acid, which leads to a yellow triphenylcarbenium salt. During this reaction, however, the chemical structure of the chromophore is completely changed, whereas

the chromophore of a genuine halochromic compound holds its chemical structure on the addition of an electrolyte. In principle, all solvatochromic compounds should be also halochromic because addition of an electrolyte to solutions of solvatochromic compounds changes the ionic strength and, hence, the solvation capability of the surrounding medium. More detailed, recent studies on the halochromism of solvatochromic compounds revealed that depending on the chemical structure of the indicator molecule, their halochromism is mainly determined either by the cations or by the anions of the salt added, leading to so-called *cationic or anionic halochromism*.^{156b} The negatively solvatochromic dyes **36**,^{160f} **42–44**,¹⁸⁴ and **48**^{156b} exhibit a typical cation-determined genuine halochromism, whereas the positively solvatochromic dye **34**¹⁵⁶ shows a characteristic anion-determined halochromism (cf. Table 1). Electrolyte solutions are important reaction media.³⁰² Therefore, the empirical determination of their solvation capability by means of solvatochromic and halochromic indicator molecules gains in importance. The determination of $E_T(30)$ values of the solvent/salt systems given in Table 4 are first attempts in this direction. It should be added that the determination of $E_T(30)$ values for pure, liquid salts is also possible (cf. solvents nos. 335–353 in Table 2).

Finally, indicator dyes such as **36** have also been used for the empirical determination of the polarity of microheterogeneous media (Table 5). For the use of other probe dyes for this purpose, see for example refs 136c, 150, 227, and 303–308. Amphiphilic molecules such as surfactants can self-associate to a variety of structured assemblies in aqueous solution, e.g. micelles (inverted micelles in nonpolar solvents), vesicles, and bilayers.⁴² A normal micelle consists of three different parts: the nonpolar interior, the hydrocarbon core, and the hydrophilic charged headgroups located at the micelle/water interface. The micropolarity of these different micellar regions can be probed by means of reporter dye molecules such as **36** (Table 5) and others, which are incorporated into the micellar system. For example, the spectroscopic probe molecule **36**, invariably solubilized in the micelle/water interface, senses changes in micropolarity caused by salt addition, variation of surfactant chain length and concentration, counterion, and temperature—and is therefore a useful rod for the study of the interface polarity of micellar and other systems. It has been demonstrated²⁷⁸ that $E_T(30)$ values can provide a quantitative measure of the surface potential of cationic micelles. The microheterogeneous systems studied so far with the solvatochromic dye **36** are collected in Table 5.

Solvatochromic probe molecules such as **36**^{161,177d} and others^{80,309–311} have also been used for the characterization of the surface polarity of solids, which are used as adsorbents in chromatography.

C. Multiparameter Approaches

In applying the aforementioned, spectroscopically derived empirical parameters to the correlation analysis of solvent effects, it is tacitly assumed that the contribution of the various, nonspecific and specific, intermolecular forces to the overall interaction be-

tween solvatochromic probe and solvent molecules is the same as in the interaction between the solute and solvent of interest in the particular solvent-dependent process under investigation. The successful application of the $E_T(30)$ values in correlation analysis of a great variety of solvent-dependent processes demonstrates that this is often the case. However, according to the chemical structure of the solvatochromic probe molecule **36**, this dye is not capable of interacting specifically and significantly with EPD solvents. That is, the Lewis basicity of solvents is not registered by this probe, whereas the solvent Lewis acidity is. In order to overcome this drawback, the two-parameter eq 5 has been introduced,³¹² which includes, as second empirical parameter, the donor number (DN) of Gutmann et al.^{9,47k,313,314} as measure of the Lewis basicity of solvents:

$$XYZ = (XYZ)_0 + \alpha E_T(30) + \beta \text{DN} \quad (5)$$

The donor number is obtained by measuring the heat of reaction of the solvent with the strong Lewis acid SbCl_5 when these reactants are dissolved in 1,2-dichloroethane. XYZ and $(XYZ)_0$ are the values of the solvent-dependent physicochemical property of the solute under investigation (e.g. $\log K$, $\log k$, $h\nu$, etc.) in a given solvent and in the gas phase (or in an inert solvent), respectively. α and β are the regression coefficients describing the relative sensitivity of the solute property XYZ to electrophilic (Lewis acidic) and nucleophilic (Lewis basic) solvent properties, respectively. By means of eq 5, a multitude of $E_T(30)$ correlations, e.g. such as with $^{23}\text{Na}^+$ NMR chemical shifts ($\beta = 85\text{--}100\%$) and enthalpies of ion solvation ($\beta = 11\text{--}72\%$), have been significantly improved.³¹² According to eq 5, good correlations between XYZ and $E_T(30)$ alone can only be expected if $\beta \approx 0$. That is, the solvent Lewis basicity should not be important to the solute/solvent interactions in these cases.

The success of eq 5 in improving $E_T(30)$ correlations is in agreement with an interesting finding made by Swain et al.^{315,316} A statistical evaluation of 1080 data sets for 61 solvents and 77 solvent-sensitive reactions and physicochemical properties taken from the literature revealed that most solvent effects can be rationalized in terms of only two complementary solvent property scales, i.e. A_j , meaning the solvent's anion-solvating tendency or *acity*, and B_j , meaning the solvent's cation solvating tendency or *basity*, both combined in eq 6:^{315,316}

$$XYZ = (XYZ)_0 + a_i A_j + b_i B_j \quad (6)$$

A_j and B_j characterize the solvent j , whereas XYZ and $(XYZ)_0$, as well as a_i and b_i , depend only on the solvent-sensitive property i under study. The terms *acity* and *basity* were chosen because, although they are obviously kinds of acidity and basicity, they are neat (bulk) solvent properties involved in solute solvation. The acidity and basicity of solvents pertain to the complete transfer of a proton from solvent to solute (acidity) or vice versa (basicity), forming a new charged chemical species. Such a process is beyond the normal meaning of solvation: a loose adduct formation between solute and solvent molecules (e.g.

via H bonding or dipole/dipole interactions), without changing the chemical integrity of the solute. The sum ($A_j + B_j$) is considered as a new measure of solvent polarity in terms of the overall solvation of a solvent.³¹⁵ For the solvent-dependent light absorption on which the $E_T(30)$ values are based, $a_i = 30.36$ and $b_i = 4.45$ ($a_i/b_i = 6.8$), thus demonstrating that the $E_T(30)$ values are mainly related to the solvent acidity, and not the solvent basicity.

Analogous considerations can be made for other empirical solvent polarity parameters derived from solvatochromic dyes as given in Table 1. A great variety of multiparameter treatments of solvent effects have been developed, using not only UV/vis/near-IR spectroscopically derived empirical parameters, but also parameters based on equilibrium and kinetic measurements as well as on other spectroscopic methods (e.g. from IR, NMR, and ESR measurements). Multiparameter treatments of solvent effects have been reviewed.^{1,47e-f,h-k,52,313c,317,318} Multiparameter equations of this kind are still manifestations of linear free-energy relationships.^{1,54-57} A statistical analysis of the problem how many significant solvent parameters are necessary for a complete quantitative description of solvent effects by means of multiparameter equations has been recently given by Palm et al.³⁴⁵ In the following, only multiparameter treatments based on solvatochromic probe molecules will be mentioned.

The reason for the introduction of multiparameter equations is the observation that solute/solvent interactions, responsible for the solvent influence on equilibria, rates, and absorptions, are caused by a multitude of nonspecific (ion/dipole, dipole/dipole, dipole/induced dipole, instantaneous dipole/induced dipole) and specific (H bonding, EPD/EPA interaction) intermolecular forces between solute and solvent molecules. Is it then possible to develop individual empirical parameters for each of these distinct interaction mechanisms and combine them into a multiparameter master equation such as eq 7:

$$XYZ = (XYZ)_0 + aA + bB + cC + \dots \quad (7)$$

where the regression coefficients describe the sensitivity of solute property XYZ to the different solute/solvent interaction mechanisms and help to unravel the observed overall solvent effect into its various contributions? This appealing concept depends on the possibility of finding solvatochromic (or other) probe molecules which interact with solvents by only one of the existing intermolecular solute/solvent interaction mechanisms—and this is not so easy to achieve!

One of the most ambitious, and very successful, quantitative treatments of solvent effects by means of a multiparameter equation such as eq 7 is that introduced by Kamlet and Taft in 1976³¹⁹ and called *linear solvation energy relationship* (LSER).^{47e,53,139} Using three UV/vis spectroscopically derived solvatochromic parameters, π^* , α , and β , eq 8 was estab-

$$XYZ = (XYZ)_0 + s(\pi^* + d\delta) + a\alpha + b\beta + m\delta_H^2 \quad (8)$$

lished, where $(XYZ)_0$, s , a , b , and m are solvent-

independent coefficients characteristic of the process under study and indicative of its susceptibility to the solvent properties π^* , α , β , and δ_H^2 .

The solvatochromic parameter π^* measures the exoergic effects of solute/solvent, dipole/dipole, and dipole/induced dipole interactions. That is, it measures the ability of a solvent to stabilize a neighboring charge or dipole by virtue of nonspecific dielectric interactions. Therefore, π^* values represent a blend of dipolarity and polarizability of the solvent. For selected solvents, i.e. nonpolychlorinated aliphatic solvents, with a single dominant bond dipole moment, π^* values are very nearly proportional to the solvent's molecular permanent dipole moment. The π^* scale is so named because it is derived from solvent effects on the $\pi-\pi^*$ absorptions of the seven nitroaromatics **15–21** (Table 1) used as primary probe molecules. The π^* scale ranges from $\pi^* = 0.00$ for cyclohexane to $\pi^* = 1.00$ for dimethyl sulfoxide. In correlating solvent effects where the blend of dipolarity and polarizability interactions is significantly different from the model process (i.e. $\pi-\pi^*$ absorption of nitroaromatics), a variable empirical polarizability parameter must be added to the first term of eq 8.^{139c} For aromatic solvents, $\delta = 1.00$, for polychlorinated (polyhalogenated?) aliphatic solvents, $\delta = 0.50$, and for all other aliphatic solvents, $\delta = 0.00$. This modification term is a less desirable, but necessary feature of the parameter π^* . π^* values are measured directly and are the mean results for the seven indicator solutes **15–21**, which are supposed to be insensitive to specific HBD and HBA interactions with solvents.

The π^* scale has been recently improved by means of a new thermosolvatochromic comparison method^{47j,272,273} and by using another set of primary solvatochromic indicator dyes (i.e. dyes **22–27** in Table 1).^{47h,147} For a further discussion of the π^* values, their shortcomings and improvements, see section V.A of this review, particularly eq 1.^{47h,47j,272,273,318} According to eq 1, π^* values can be simply determined by means of only one primary indicator, i.e. 4-methoxynitrobenzene.^{47j,272,273} For solvents which are not transparent in the absorption range of 4-methoxynitrobenzene, a secondary indicator, 4-(dimethylamino)nitrobenzene, can be used. Further procedures for the calculation of π^* values have been recently collected by Marcus.³¹⁸

The solvatochromic parameter α in eq 8 is a quantitative, empirical measure of the ability of a bulk solvent to act as a hydrogen-bond donor (HBD) toward a solute.^{47e,139,319} The *solvatochromic comparison method* for the determination of α values consists of the comparison of solvent-induced shifts of the longest wavelength $\pi-\pi^*$ absorption band of two similar (ideally homomorphic) probe molecules, one of which cannot act as hydrogen-bond acceptor toward HBD solvents [(e.g. 4-methoxynitrobenzene (**16**)], whereas the other can (e.g. the betaine dye **36**): Ar-O⁻ in **36** is a better hydrogen-bond acceptor than Ar-OCH₃ in **16**. According to the similarity (or homomorphism) of the two probe molecules, a plot of the absorption wavenumbers of **36** against those of **16** gives, for non-HBD solvents, a straight reference line of the type $\tilde{\nu}(\mathbf{36}) = a\tilde{\nu}(\mathbf{16}) + b$. HBD

solvents fall off (in this case above) the line because of stronger hydrogen bonding of HBD solvents to the betaine **36** than to 4-methoxynitrobenzene (**16**). This supplementary enhanced band shift, induced in betaine **36** relative to **16**, is denoted $\Delta\Delta\tilde{\nu}(\mathbf{36}-\mathbf{16})$ and can be calculated from the deviation of HBD solvents from the reference line via equation $\Delta\Delta\tilde{\nu}(\mathbf{36}-\mathbf{16}) = [\alpha\tilde{\nu}(\mathbf{16}) + b] - \tilde{\nu}(\mathbf{36})$ for each HBD solvent. By the same solvatochromic comparison method, various other pairs of probe molecules have been investigated and, eventually, α values were arrived at by a process of successive approximations and statistical calculations.^{47e,47j,139f} α values are zero for non-HBD solvents such as aliphatic and aromatic hydrocarbons. For aliphatic alcohols, $\alpha \approx 0.5-1.0$ ($\alpha = 0.98$ for methanol), and for fluoro-substituted aliphatic alcohols and phenols, $\alpha > 1.0$, reaching a maximum with $\alpha = 1.96$ for hexafluoroisopropyl alcohol.³¹⁸ Further procedures for their determination and a collection of α values have been recently given by Marcus.^{318,320}

The solvatochromic parameter β in eq 8 is a quantitative, empirical measure of the ability of a bulk solvent to act as a hydrogen-bond acceptor (HBA) or electron-pair donor (EPD) toward a solute, forming a solute-to-solvent hydrogen bond or a solvent-to-solute coordinative bond, respectively.^{47e,139,319} The solvatochromic comparison method used to determine β values consists (analogous to the determination of α values) of the comparison of solvent-induced shifts of the longest wavelength $\pi-\pi^*$ absorption band of two homomorphic probe molecules, one of which cannot act as hydrogen-bond donor toward solvents [e.g. 4-(diethylamino)nitrobenzene (**17**); cf. Table 1], whereas the other can (e.g. 4-aminonitrobenzene, ANB): Ar-NH₂ in ANB is a better hydrogen-bond donor than Ar-N(C₂H₅)₂ in **17**. The term *homomorphic* molecules was first introduced by Brown et al.³²¹ Molecules having the same, or closely similar, molecular size and geometry are called *homomorphs*; these should have similar physical properties (e.g. UV/vis spectra). According to the homomorphism of the two probe molecules, a plot of the absorption wavenumbers of ANB against those of **17** gives, for non-HBA solvents, a straight reference line of the type $\tilde{\nu}(\text{ANB}) = \alpha\tilde{\nu}(\mathbf{17}) + b$. HBA solvents fall below this line because of stronger hydrogen bonding between HBA solvents and ANB, as compared to HBA solvents and **17**. This supplementary, enhanced band shift, denoted $\Delta\Delta\tilde{\nu}(\text{ANB}-\mathbf{17})$, can be calculated from the deviation of HBA solvents from the reference line via equation $\Delta\Delta\tilde{\nu}(\text{ANB}-\mathbf{17}) = [\alpha\tilde{\nu}(\mathbf{17}) + b] - \tilde{\nu}(\text{ANB})$ for each HBA solvent. The same method has been used for other pairs of homomorphic molecules (e.g. 4-nitrophenol/4-nitroanisole). Eventually, β values were again arrived at by a process of successive approximations and statistical calculations.^{47e,47j,139f} The β scale was later improved by Laurence et al. by determining more precise reference lines and replacing 4-(diethylamino)nitrobenzene (**17**) by 4-(dimethylamino)nitrobenzene as secondary probe because of an irregular correspondence between the vibrational structure in the absorption bands of ANB and **17**.^{47j,140a}

The β scale was fixed by setting $\beta = 0.0$ for cyclohexane and $\beta = 1.0$ for hexamethylphosphoric triamide (HMPT). β values are zero for non-HBA and non-EPD solvents such as aliphatic hydrocarbons; however, for aromatic hydrocarbons, $\beta \approx 0.1$. For aliphatic ethers, $\beta \approx 0.3-0.5$ ($\beta = 0.47$ for diethyl ether) and for aliphatic alcohols, $\beta \approx 0.7-0.9$ ($\beta = 0.66$ for methanol). For aliphatic amines, $\beta \approx 0.5-0.7$ ($\beta = 0.71$ for triethylamine), reaching a maximum with $\beta = 1.43$ for 1,2-diaminoethane.³¹⁸ Further procedures for their determination and a compilation of β values have been recently given by Marcus.³¹⁸

In addition to the solvatochromic parameters π^* , α , and β , which represent the exoergic solute/solvent interactions, eq 8 includes a fourth so-called cavity term, δ_H^2 , which represents a physical solvent quantity called cohesive pressure (or cohesive energy density).³²² This quantity is related to Hildebrand's solubility parameter, δ_H , which is given by $\delta_H = (\Delta H^\circ - RT/V_m)^{1/2}$, where ΔH° is the molar standard enthalpy of vaporization of the solvent to a gas of zero pressure, and V_m is the molar volume of the solvent.³²³ The squared solubility parameter corresponds to the endoergic process of separating the solvent molecules to provide a suitably sized enclosure for the solute and measures the work required to produce a cavity of unit volume in the solvent. This term is related to the tightness or structuredness of solvents as caused by intermolecular solvent/solvent interactions. The resulting association of solvent molecules in the liquid state depends on their chemical structure and can be quantified by means of their cohesive pressure.^{1,323} It has been shown that this cavity term is only poorly correlated with the other three parameters of eq 8, which is an important precondition for its inclusion into eq 8.³¹⁸

Most of the reported linear solvation energy relationships are simpler than that indicated by eq 8. For example, if the solvent-induced change of the XYZ property does not involve the creation of a cavity or a change in cavity volumes between different states (initial and transition state; ground and excited state), the term $m\delta_H^2$ drops out. This is notably the case for UV/vis/near-IR absorptions because electronic transitions are hardly accompanied by a change in molar volume of the absorbing ground-state molecule on excitation. Thus, for the correlation of solvent effects on spectra, eq 8 can be correspondingly simplified. If only non-HBD solvents are considered, the α term in eq 8 drops out. Conversely, if the solutes are not hydrogen-bond donors or Lewis acids, the β term drops out of eq 8. In this way, depending on the chemical structure of solutes and solvents, the four-parameter eq 8 can be reduced to a three-, two-, and even one-parameter equation, sometimes leaving π^* as the only remaining parameter.

Equation 8 applies to the influence of *different solvents* on the properties XYZ of a *single solute* (e.g. absorption spectra, reaction rates, equilibrium constants, etc.). Conversely, eq 8 can also be used to correlate the properties XYZ of a set of *different solutes* in a *single solvent* (e.g. solubilities, partition coefficients, etc.), provided eq 8 is changed into eq

9, where all of the explanatory parameters (π_2^* , α_2 ,

$$XYZ = (XYZ)_0 + s\pi_2^* + a\alpha_2 + b\beta_2 + mV_2/100 \quad (9)$$

β_2 , V_2) are now denoted with a subscript 2 to indicate that they represent now solute parameters, not solvent parameters.³²⁴ In eq 9, π_2^* denotes the dipolarity/polarizability of the species acting as an infinitely dilute solute. α_2 and β_2 represent the hydrogen-bond acidity and hydrogen-bond basicity, respectively, of the same species, acting again as an infinitely dilute solute. V_2 is the solute molar volume and is divided by 100 so that the cavity term covers roughly the same numerical range as the π_2^* , α_2 , and β_2 parameters, which simplifies the evaluation of the contributions of the various terms in eq 9.³²⁴

The methodology of *linear solvation energy relationships* by means of eqs 8 and 9 has been used to unravel, identify, and evaluate the individual solute/solvent interactions that determine the solvent effects of numerous examples.³²⁵ In three series entitled *Linear Solvation Energy Relationships*,³²⁶ *Solubility Properties in Polymers and Biological Media*,³²⁷ and *Solute-Solvent Interactions in Chemistry and Biology*,³²⁸ the usefulness of this solvatochromically derived concept has been impressively demonstrated. Further developments of this methodology, particularly with respect to its application in chromatography, have been reviewed by Abraham,³²⁹ Carr,⁸⁰ and Poole et al.³³⁰ The use of computer-calculated quantum chemical properties as surrogates for the experimentally determined solvatochromic parameters, as described above, has been recently reviewed by Cramer et al.³³¹ The empirical solvatochromic parameters π^* , α , β , etc. can be replaced by theoretically derived descriptors to give a so-called *Theoretical Linear Solvation Energy Relationship* (TLSE), which may be used in a predictive fashion like other LFE relationships.³³¹

With eq 10, another multiparameter equation for the correlation of solvent effects on physicochemical properties XYZ has been recently proposed by Drago.^{332,333} Equation 10 includes, with the $E_A^*E_B$ and

$$XYZ = (XYZ)_0 + E_A^*E_B + C_A^*C_B + pS' \quad (10)$$

$C_A^*C_B$ terms, the well-known E/C equation of Drago³³⁴ that describes the specific EPD/EPA interactions between a Lewis acid A and a Lewis base B. The acid A and the base B are both characterized by two empirical parameters E and C , and it is assumed that the standard enthalpy of a 1:1 Lewis acid/base interaction can be divided into two terms $E_A^*E_B$ and $C_A^*C_B$, which are said to correspond to tendencies of electrostatic and covalent contributions in the acid/base interaction, respectively.³³⁴ The E/C equation, initially derived for all kinds of Lewis acid/base interactions, is also applicable to corresponding specific solute/solvent interactions. The asterisks in eq 10 indicate that the acceptor parameters are for a physicochemical property, while the E_B and C_B parameters are from the enthalpy scale.

If one considers only nonspecific solute/solvent interactions, the E/C terms in eq 10 drop out to give

eq 11, where S' represents an empirical parameter

$$XYZ = (XYZ)_0 + pS' \quad (11)$$

measuring only the nonspecific solvating ability of solvents.³³² Using a least squares minimization program, the measured physicochemical properties XYZ of systems that cannot undergo specific interactions with donor (EPD) solvents, have been fitted to eq 11. A total of 366 relevant literature values were selected; 34 solvents and 82 probes were utilized (among them probes **2**, **17**, **36**, **53**, and **63**). In order to get a solution for the p , S' , and $(XYZ)_0$ values from 366 simultaneous equations, the S' value for dimethyl sulfoxide has been fixed ($S' = 3.00$) to anchor the scale. The selected solvent-dependent reference processes include not only electronic transitions of negatively and positively solvatochromic probe molecules, but also ¹⁹F and ¹⁵N NMR chemical shifts as well as ESR hyperfine coupling constants.³³² S' values are known for 46 solvents and range from 1.11 for cyclohexane to 3.07 for nitromethane. The S' scale is considered as a generalized, single-parameter scale of nonspecific solvent polarity, which excludes specific solute/solvent interactions. In particular were excluded (a) concentrated probe solutions, in order to avoid solute/solute interactions (as in *n*-hydrocarbons which favor solute aggregation), (b) specific EPD/EPA interactions (e.g. between π solutes and π solvents as well as between EPD donors and haloalkanes), and (c) dipolar solvents that exist as rotamers with variable solvating abilities (e.g. 1,2-dichloro- and 1,2-dimethoxyethane). The fact that the same S' values can be used for correlating physicochemical properties of different probe molecules with a wide variety of solute shapes and sizes has led to the proposal of a so-called dynamic cavity model.³³² According to this, solvent molecules rearrange to form cavities to accommodate the solute molecules, thus maximizing the nonspecific solute/solvent interactions. The cavity size varies with the dimension of the solute molecule and with the strength of the nonspecific solute/solvent interactions, with strong interactions leading to short solute/solvent distances. In this way, solvent dipole reorientation and induced solvent dipoles make up the effective internal relative permittivity of the cavity, which differs from the relative permittivity of the pure bulk solvent. For this reason, molecular microscopically derived empirical solvatochromic parameters usually differ from macroscopically measured physical parameters of the pure solvents such as dipole moment, relative permittivity, or refractive index. When solvent/solvent and/or solute/solute interactions are of comparable strength to solute/solvent interactions, aggregation of the solute occurs. When they are much larger, insolubility of the solute results.³³²

VI. Interrelation between Empirical Solvent Polarity Parameters

As already mentioned in section V.A, for a number of reasons only a few of the solvatochromic dyes compiled in Table 1 meet the requirements for a good indicator molecule, probing empirically the polarity

Y and $E_T(30)$ values are interchangeable, at least for the pure solvents of Figure 3. $Y/E_T(30)$ plots for binary solvent mixtures show some curvature because of different preferential solvation of both probe solutes,^{47a,158} whereas corresponding Y/Z plots give linear relationships in several solvent mixtures.^{51,204}

Extensive compilations of possible and reasonable binary linear correlations between various single-parameter scales of solvent polarity, mainly based on UV/vis/near-IR measurements, have been recently given by Buncel et al.^{47h} and Marcus.³¹⁸ Further examples of more or less good mutual linear correlations (with $r > 0.8$) between single parameters are the pairs $E_T(30)/\alpha$, AN/α , Z/α , $acidity/\alpha$, $E_T(30)/AN$, $E_T(30)/acidity$, Z/AN , $acidity/AN$, DN/β , and $basity/\pi^*$,³¹⁸ where AN and DN are Gutmann's solvent acceptor and donor numbers (cf. eq 5), respectively,³¹³ and acidity and basity are as defined in eq 6.³¹⁵ A comparison of π^* (cf. entries 15–21 in Table 1) and π_{az0}^* values (cf. entries 22–27 in Table 1) with 20 other solvent polarity scales has been made by Buncel et al.^{47h} Further binary correlations can be found in refs 47a,e,i,k, 53b, and 64a.

Of particular interest are correlations between single parameters of solvent polarity and constituents of multiparameter equations such as eq 8, which should provide insight into the detailed interaction mechanisms between the solvatochromic indicator solute and the solvents. Application of eq 8 to the correlation of $E_T(30)$ values leads to eq 12, where the $m\delta_H^2$ term has been dropped for the reasons already mentioned (no volume change during electronic transitions).

$$E_T(30) = [E_T(30)]_0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (12)$$

For a set of $n = 100$ various solvents, for which $E_T(30)$, π^* , α , and β are available, eq 13 has been

$$E_T(30) = 30.2 + 12.99(\pi^* - 0.21\delta) + 14.45\alpha + 2.13\beta \quad (13)$$

recently calculated by Marcus,³²⁰ with a multiple correlation coefficient as high as $r = 0.987$ and a standard deviation of $\sigma[E_T(30)] = 1.25$ kcal/mol. By using the normalized, dimensionless E_T^N values instead of $E_T(30)$ values (in kcal/mol), eq 13 changes into eq 14, with the same statistical parameters as for eq 13, except for $\sigma[E_T] = 0.039$.³²⁰

$$E_T^N = -0.015 + 0.401(\pi^* - 0.211\delta) + 0.446\alpha + 0.066\beta \quad (14)$$

Although statistically significant, the regression coefficients of the terms $d\delta$ and $b\beta$ in eqs 13 and 14 are comparatively small and the two terms can be disregarded without worsening the correlation too much. Obviously, the solute/solvent interactions between betaine dye **36** and HBA or EPD solvents play only a minor role. Therefore, eq 13 can be simplified to the two-parameter eq 15, where $n = 100$,

$$E_T(30) = 30.2 + 12.35\pi^* + 15.90\alpha \quad (15)$$

$r = 0.967$, and $\sigma[E_T(30)] = 1.95$ kcal/mol.³²⁰ Very

recently, eq 15 has been recalculated for a majority of $n = 166$ (!) solvents to give eq 16,³¹⁸

$$E_T(30) = 31.2 + 11.5\pi^* + 15.2\alpha \quad (16)$$

with $r = 0.979$ and $\sigma[E_T(30)] = 2.1$ kcal/mol.

According to eqs 15 and 16, the mutual interaction between solvatochromic probe (**36**) and solvent molecules is mainly determined by a blend of nonspecific dipole/dipole, dipole/induced dipole, instantaneous dipole/induced dipole (i.e. dipolarity/polarizability) interactions (as measured by π^*), and specific solute/HBD solvent (i.e. type-A hydrogen bonding³¹⁹) interactions (as measured by α). The ratios of the regression coefficients of α and π^* in eqs 15 and 16 are $\alpha/\pi^* = 1.29$ and 1.32 , respectively. Hence, the sensitivity of $E_T(30)$ to α is slightly larger than to π^* . In HBD solvents, $E_T(30)$ values measure, therefore, mainly the HBD acidity and Lewis acidity of the solvents. In non-HBD solvents with $\alpha = 0$, the $E_T(30)$ values are mainly determined by the nonspecific dipolarity/polarizability interactions.

The observation (a) that $E_T(30)$ values remain almost constant (31.0 ± 0.2 kcal/mol) for tetramethylsilane and 10 alkanes (cf. entries 1–14 in Table 2), in spite of the fact that the refractive index n ranges from 1.35 for 2-methylbutane to 1.48 for *cis*-decalin, and (b) that $E_T(30)$ values are not correlated with the polarizability function $f(n) = (n^2 - 1)/(2n^2 + 1)$ for aromatic, polychloro-substituted and various other solvents,¹⁶² shows that there exists a compensation of solvent-induced hypsochromic band shifts caused by induction forces and bathochromic band shifts caused by dispersion forces.¹⁶² Dispersion forces alone would always lead to bathochromic band shifts because molecules in the electronic excited state possess higher polarizabilities than that in the ground state. Therefore, for all negatively solvatochromic dyes in Table 2, this bathochromic band shift caused by dispersion interactions is overcompensated by the hypsochromic band shifts stemming from all other solute/solvent interactions.

As for the $E_T(30)$ values given in eqs 13, 15, and 16, for the Z values of Kosower,⁵¹ analogous multiparameter equations such as eq 17 have been recently established by Marcus for $n = 55$ solvents with $r = 0.971$ and $\sigma[Z] = 2.9$ kcal/mol.^{318,320}

$$Z = 55.9 + 10.2\pi^* + 20.6\alpha \quad (17)$$

In eq 17, the ratio α/π^* is, with 2.02, much larger than that in eqs 15 and 16. This clearly shows that the solvation of the ion pair **53** (particularly of its iodide ion) by HBD solvents is much stronger than the hydrogen bond-mediated solvation of the phenolate moiety in the betaine dye **36**, thus leading to the greater solvatochromic sensitivity of **53** as compared to **36**, at least for HBD solvents (cf. Figure 2).

Further correlations of single parameters of solvent polarity within the framework of multiparameter equations (particularly with eq 8) and their interpretation and application can be found in refs 47e,h–j, 52, 53b, 318, 320, and 326–328. Sometimes, such multiparameter correlations have even been used to recalculate single parameters of solvent polarity.^{318,320} A multivariate statistical factorial analysis of a data matrix of four physicochemical solvent properties for

22 solvents [i.e. dipole moment, molar refraction, Kirkwood function $f(\epsilon_r) = (\epsilon_r - 1)/(2\epsilon_r + 1)$, and Hildebrand's solubility parameter] gave four independent, orthogonal factors F_i , the linear combination of which, according to $XYZ = (XYZ)_0 + a_1F_1 + b_2F_2 + \dots$, was able to reproduce the data set.³³⁷ An analysis of various solvent polarity parameters by means of these mathematically derived four factors has been given by Chastrette et al.³³⁷ Solvatochromic parameters have also been used for the classification of organic solvents by means of multivariate statistical methods.³³⁸⁻³⁴²

The relative proportion of the various contributions to the overall solute/solvent interaction, as described by eqs 13-17, is quite often found in other solvent-dependent processes. This explains the unexpected success in applying single solvent polarity parameters, such as Z and $E_T(30)$, in correlating solvent effects. A correlation of solvent effects with a single parameter of solvent polarity gives usually a first insight into the solute/solvent interactions of the process under study, and allows often at least a semiquantitative calculation of solvent-dependent rate or equilibrium constants, spectral absorptions, etc. For a more detailed analysis of solvent effects under study, however, it is sometimes better to apply a multiparameter equation, where the number of parameters which should be taken into account depend on the complexity of the respective solute/solvent, solvent/solvent, and solute/solute interactions.

The solvatochromic and other multiparameter approaches in correlating solvent effects have, however, some serious short-comings. First, the separation of solvent effects into various additive contributions according to eq 7 is somewhat arbitrary, since different solute/solvent interaction mechanisms can cooperate in a nonindependent way. For example, the π^* parameter in eq 8 is still a mixed parameter, responsible for dipolarity and polarizability solute/solvent interactions, it being not possible to devise independent descriptors for these solvent properties separately.

Second, the proper choice of the best-suited parameter for each kind of supplementary solute/solvent interactions is critical, and not yet finally solved. Up to now, the most successful multiparameter treatment of solvent effects is certainly the *solvatochromic comparison method* according to eq 8, as introduced by Kamlet and Taft in 1976.^{47e,53,139,319,326-328}

Third, to establish a multiparameter equation, so many experimental data points are usually necessary in order to calculate all regression coefficients in a statistically sound way, that there is often no room left for the desirable predictions of solvent effects by extrapolation or interpolation.

If one weighs one thing against the other, one should be aware of the helpful remark made by the Austrian philosopher Karl Popper in his autobiography:³⁴³ "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..."^{343,344}

VII. Summary and Conclusions

In order to understand solvent effects on chemical reactions and physical absorptions in a more quantitative way, a multitude of empirical solvent polarity scales, derived from various physicochemical processes, have been proposed during the last few decades.^{1,47} Of these solvent scales, the most comprehensive and the easiest to determine are those based on the solvatochromic method. In Table 1, a compilation of positively and negatively solvatochromic as well as some selected solvatofluorochromic compounds has been given, which are suitable as indicator molecules for the empirical determination of solvent polarity within the framework of linear free-energy relationships. Some of these have been used to introduce comprehensive solvent scales, others are possible and promising candidates for this purpose. It was not possible to include in Table 1 all solvatochromic compounds described in the literature. The preconditions for being a good solvatochromic probe molecule, defined above, should be taken into account for the development of further UV/vis/near-IR spectroscopically derived empirical parameters of solvent polarity.

Among the single-parameter approaches, the $E_T(30)$ scale as one of the more comprehensive solvent scales (cf. Tables 2-5) has been exemplarily discussed at some length. The popular solvatochromic comparison method, introduced by Kamlet and Taft and further developed by Abboud, Abraham, Carr, and Laurence, has been used to demonstrate the advantages of a multiparameter treatment of solvent effects. This was followed by a comparison of some of the solvatochromic solvent scales, which shows that many of the empirical parameters are linearly related to each other, thus demonstrating the similarity of the intermolecular solute/solvent interactions in many cases.

Taking into account the wide variation in chemical structure of the probe molecules used for construction of a solvent scale, the question arises which of them are the most representative compounds in modeling solute/solvent interactions, leading to a more or less universal solvent polarity scale. Because solute/solvent interactions do not depend on the solvent structure alone, but always also on the chemical structure of the probe solute, the establishment of a universal, generally valid solvent polarity scale seems to be unattainable.^{47h,147}

From a more puristic physical-organic chemist's point of view, the application of empirical parameters of solvent polarity has certainly its inherent weaknesses and limitations. In using such parameters, one should always be aware of the fact that one simply compares the solvent effect under study with another solvent-dependent model process. So, the solvent effect under study can be understood qualitatively and quantitatively in that way and to that extent as the solvent influence on the model process is known. However, this kind of procedure is very common in chemistry. For example, the well-known Hammett equation for the calculation of substituent

effects on reaction rates, equilibria, and absorptions, introduced by Hammett in 1937,⁵⁸ uses the ionization of meta- and para-substituted benzoic acids in water at 25 °C as a reference process. Using Hammett's substituent constants is nothing else than comparing the substituent effect under study with the ionization of substituted benzoic acids. Although introduced 57 years ago, Hammett substituent constants and their refinements are still popular and in use.⁵⁵⁻⁵⁸ Whether empirical solvent polarity parameters will survive for a correspondingly long time is questionable in view of the large progress which has been recently made in the calculation of solute/solvent interactions by means of modern quantum chemical methods. However, for most chemists working in the laboratory, who are daily confronted with the proper choice of a suitable solvent for the planned reaction, empirical parameters of solvent polarity will certainly be of lasting importance.

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