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Quantitative Measures of Solvent Polarity

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1. Introduction

In 1890, W. Ostwald wrote:

> *Almost all the chemical processes, which occur in nature, whether in animal or vegetable organisms or in non-living surface of the Earth ... take place between substances in solution.*

Simplistically, “solutions” can be defined as homogeneous liquid phases consisting of more than one substance in variable ratios, where one of the substances, the so-called “solvent” (which could itself be a mixture), is treated differently from the other substances, which are called “solutes”. Usually, the solute(s) is/are the minor component(s) and the solvent is the component in excess.

In 1862, Berthelot and de Saint-Giles, after thorough studies on the esterification of acetic acid with ethanol, noted for the first time the influence of solvents on the rates of chemical reactions.[1] In 1890, Menschutkin asserted that a reaction cannot be separated from the medium in which it has occurred.[2] He considered that the influence of solvents is primarily related to their chemical structure rather than their physical properties and postulated relationships between the rates of reactions and solvent structure.

Later, it became obvious that a solvent should not be considered only as a macroscopic continuum characterized purely by physical constants but also as a discontinuum consisting of individual mutually interacting solvent molecules. These macroscopic and microscopic approaches must be considered together (not separately) as defining the general concept of “solute-solvent interactions”. This concept involves and influences all of the following: (i) macroscopic (bulk) physical properties, including refractive index, relative permittivity, density, thermodynamic characteristics and more; (ii) microscopic intermolecular forces, including ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding, electron pair donor−electron pair acceptor interactions (EPD/EPA), and solvophobic interactions; (iii) solvation in multicomponent systems, involving selective solvation and micellar solvation (solubilization); and (iv) “chemical” solvation related to ionization and dissociation processes.

Factors i−iv are collectively well-known as “solvent effects” and are conventionally ascribed to a solvent’s “polarity”. The term “polarity” is usually related to the capacity of a solvent for solvating dissolved charged or dipolar species. “Polarity” is easy to comprehend qualitatively, but substantial difficulties arise with (i) its precise definition and (ii) its quantitative measurement.

Reichardt[3] defined “solvent polarity” as “the overall solvation capability (or solvation power) for reactants and activated complexes as well as for molecules in the ground and excited states, which in turn depends on the action of all possible, specific and nonspecific, intermolecular forces between solvent and solute molecules, including Coulomb interactions between ions, directional interactions between dipoles, and inductive, dispersion, hydrogen-bonding, and charge-transfer forces, as well as solvophobic interactions. Only those interactions leading to definite chemical alterations of the solute molecules through protona-

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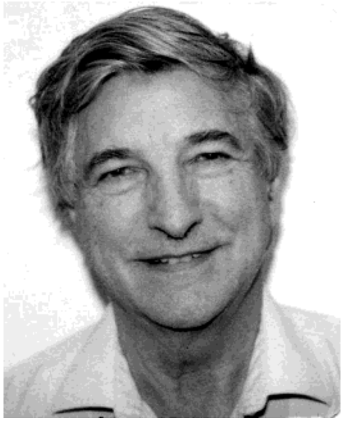

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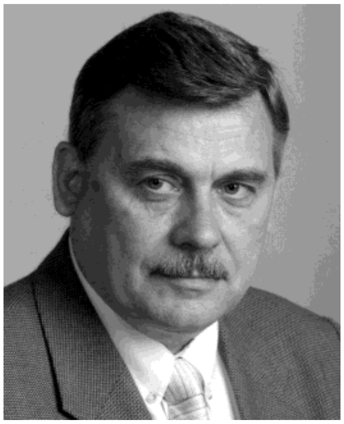
Kaido Tämm, born in Tartu, Estonia, received his M.S. degree in chemistry at the University of Tartu, in 2001. In 2002 he joined Prof. Alan R. Katritzky’s computational chemistry group at the University of Florida.

tion, oxidation, reduction, complex formation, or other chemical processes are excluded.” This definition already suggests that solvent polarity cannot be uniquely assessed quantitatively by any single physical constant. Furthermore, Reichardt demonstrated experimentally[3] that macroscopic dielectric constants alone are unsuitable measures of molecular-microscopic interactions. From a very general point of view, the chemical processes (i.e., the protonation by solvent) may also substantially modify the solvational capability (or solvational power) of solvents. Therefore, we would expand Reichardt’s definition of solvent polarity and do not exclude such phenomena in the further discussion.

A most important feature for the success of any planned reaction is the selection of a suitable solvent: solvents influence both chemical reactivity and reaction rates. The importance of solvent effects has long stimulated attempts to define solvent polarity in terms of empirical parameters, based on diverse solvent-sensitive reference processes. The aims of such attempts have been to obtain better parameters of solvent polarity by choosing solvent-dependent standard systems and examining the changes in parameters of that system when the solvent is changed.[3] Solvents can be classified in many ways including their polarity, acidity, electron pair or proton-donating properties, etc. Some solvent scales are defined to describe individual intermolecular interactions in liquid media; others do not separate specific properties and are referred to as general polarity scales.

The present paper focuses on available quantitative measures of solvent polarity. It reviews the different individual solvent scales (developed using pure solvents and based on empirical parameters) and the interrelations among them. The last section summarizes briefly the present position and the potential for future development of the concept of solvent polarity.

Tarmo Tamm (born in 1974) is a lecturer at the Institute of Physical Chemistry at the University of Tartu, Estonia. His research interests have been related to the properties and quantum chemical modeling of conducting polymers (Ph.D. degree in 2003) and the applications of QSAR/QSPR to the properties of solutions.



Mati Karelson (born in 1948) is Professor and Head of Theoretical Chemistry at the University of Tartu, Estonia. He received his Ph.D. degree in physical organic chemistry in 1975. His research has dealt with the theory of solvent effects, the foundations of QSAR/QSPR, and the development of the corresponding computer software. He is actively engaged in teaching, industrial consulting, and scientific management. He is also Courtesy Professor in Chemistry at the University of Florida.

2. Individual Solvent Scales

2.1. Brief Historical Overview of Development of Scales

The term “solvent polarity” lacks an exact definition, but it is generally used to encompass all of the intermolecular interactions of which the solvent is capable. During the past few decades, it became clear that the use, for example, of Clausius−Mossotti relative permittivity alone cannot represent completely the electrostatic solute-solvent interactions and, thus, cannot provide a reliable guide for predicting solvent effects on specific chemical reactions. Consequently, many different alternatives were proposed to measure solute-solvent interactions, resulting in a large variety of so-called “solvent polarity scales” based on diverse solvent-sensitive reference processes/empirical parameters.

Historically, the forerunners in the development of empirical scales were Grunwald and Winstein,[4] who in 1948 computed *Y* values from rate constant studies. Significant contributions to the development of solvent scales were made by Kosower,[5−7] Katritzky and co-workers,[8] Koppel and Palm,[9] Gutmann and Wychera,[10] Dimroth and Reichardt,[11] Kamlet and Taft,[12−14] Abraham,[15] and many others (see Table 1).

Choosing a model system and recording the response of one of its parameters to the change of solvent have been the essence of the development of most of these scales. The model process must be chosen with care and represent properly the interactions of the system, yet no one scale can be universal and useful for all kinds of reactions. On more theoretical considerations, the best model processes maximize solvent effects.

According to Abboud and Notario,[16] the “empirical treatment” of solvent polarity is frequently assisted by the regularities displayed in many cases by solvent effects.

Many examples of processes known to be solvent-sensitive cannot be correlated by a single empirical solvent parameter. It has been found repeatedly that the simple concept of “polarity” as a universally determinable and applicable solvent characteristic is a gross oversimplification. The solvation capability or solvation power of a solvent, which has been roughly divided into nonspecific and specific solute-solvent interactions, is the result of many different kinds of interaction mechanisms between the molecules of the solute and the solvent.

By considering a solute, SOL, and two different properties, P_1 and P_2, with the values $\{P_{10}, P_{11}, ..., P_{1i}, ...\}$ and $\{P_{20}, P_{21}, ..., P_{2i}, ...\}$, respectively, in solvents S_0, S_1, ..., S_i, ..., a solvent scale can easily be constructed. Choosing S_0 as a reference solvent, taking for each solvent, S_i, the difference $P_i = (P_{1i} - P_{10})$ could be considered to define a simple scale. If the property P_1 is a “good descriptor” of solvent effects on P_2, eq 1 or 1a holds for solvent S_i, wherein k is a constant independent of the solvents and determined only by P_2. Then p_i is the “solvent parameter” characteristic of solvent S_i.

$$P_{2i} - P_{20} = k(P_{1i} - P_{10}) \tag{1}$$

or

$$P_{2i} - P_{20} = kp_i \tag{1a}$$

Such an equation can be applied only to data for a large number of well-chosen solvents, and its success must be examined by proper statistical methods. The separation of solvent polarity into various solute-solvent interaction mechanisms is purely formal and may not be even theoretically valid as the interactions could be coupled and not operate independently of each other. However, if such a separation could be justified, the resultant parameters could be used to interpret solvent effects through such multiple correlations and provide information about the type and magnitude of interactions with the solvent. In such a case, only applications to processes that have the same relative sensitivity to various interaction mechanisms as the single solvent parameter will give a good correlation. Such multiparameter approaches to explain solvent effects on chemical and physical properties have been proposed by Katritzky et al.,[8]

Table 1. Solvent Scales Used in the Study

no.	scale[a]	no. of solvents[b]	author(s)[c]	physical background	refs[d]
			Spectroscopic Measurements		
1	AN	34	Mayer	acceptor number, derived from ^{31}P NMR of triethylphosphine oxide in different solvents	75
		52	Marcus		14
2	A_N	31	Knauer and Napier	N^{14} hyperfine splitting constants of di-*tert*-butylnitroxide free radical	76
3	B	71	Koppel and Palm	basicity from stretching frequency of CH_3OD in different solvents	9
4	B'	19	Renge and Avarmaa	O−H stretching frequency shift in cm^{-1} in phenol dissolved in CCl_4 when a nucleophile is added to form an H-bonded complexes	77
5	B-2	53	Koppel and Paju	acid-base hydrogen bond formation induced shifts of phenol OH group stretching frequency	55
6	BCo	25	Waris	ratio of the fluorescence intensities of bands I and III of the vibronic spectra of benzo(α)coronene	78
7	B_{KT}	44	Krygowski	calculated from the difference of the longest wavelength band in the UV-vis spectra measured for *p*-nitroaniline and *N*,*N*-diethyl-*p*-nitroaniline	79
8	BPe	25	Waris	relative band intensities (I/III) for benzo[*ghi*]perylene fluorescence spectra	80
9	Co	12	Nakajima	relative band intensities (I/III) for coronene fluorescence spectra	81
		25	Waris		78
10	C_p-SCS	6	Bromilow	substituent chemical shifts for the para carbon of *N*,*N*-dimethyl for the monosubstituted ($n = 21$) benzene	82
11	CTTS	16	Fox and Hayon	absorption maxima of iodide ions	83
12	Cu-λ_{max}	38	Persson	maximum absorption band of Cu(tmen)(acac)(solv)	84
13	DCo	23	Waris	ratio of the fluorescence intensities of bands I and IV of the vibronic spectra of dibenzo[α,*j*]coronene	78
14	D_S	61	Persson	donor strength decrease in symmetric stretching frequency of Hg_2Br_2, between the gas phase and solutions	38
15	$E_{(NR)}$	82	Deye and Berger	Nile red transition energy	85
16	E^*_{MLCT}	33	Manuta and Lees	solvent dependence of metal to ligand charge-transfer absorption maxima of $W(CO)_4$ with 1,10-phenanthroline	86
17	$E_{CT(\pi)}$	28	Kaim	CT spectra of $W(CO)_4$ complexes with TCNE E^*_{MLCT} (cm^{-1}) = 3000 (cm^{-1}) × $E_{CT(\pi)}$ + 12360 (cm^{-1})	87
18	$E°$ (H_2(g)/H^+(aq)	6	Persson	standard electrode potentials in volts of [H_2(g)/H^+(aq)]	84
19	E_B	53	Janowski	energy of n→p* transition in the 2,2,6,6-tetramethylpiperidine *N*-oxyl spectrum	88
20	E_{CT} (A)	23	Davis	UV charge-transfer absorption maxima of tetra-*n*-hexylammonium iodide trinitrobenzene	89
21	E_{LMCT}	6	Shepherd	energies of charge-transfer transitions of $(CN)_5FeL^{2-}$ and imidazole complexes	90
22	$E_T(30)$	362	Reichardt	molar electronic transition energy of dissolved negatively solvatochromic pyridinium *N*-phenolate betaine dye	62
23	E_T^{SO}	36	Walter and Bauer	UV-vis spectra of *N*,*N*-(dimethyl)thiobenzamide-*S*-oxide	91
24	G	21	Allerhand and Schleyer	infrared vibration shift of hydrogen bonding	39
25	H	11	Mukerjee	molar concentration of OH dipoles in (55.4 M) TEMPO	92
26	$^2J_{119Sn-117Sn}$	21	Lockhart	tin−tin spin-coupling constant ^2J(^{119}Sn-^{117}Sn) of the hexaorganodistannoxanes	93
27	K	25	Menger and Boyer	equilibrium constants for the conformational mobile (+)-*trans*-*a*-chloro-5-methylcyclohexanone	94
28	Kq^{MMA}	12	Fouassier and Jacques	quenching rate constants for the deactivation of triplet thioxanthone by methyl methacrylate	95
29	$\log \gamma K_c$	11	Pac	fluorescence quenching rate constants for naphthonitrile−olefin and furan pairs	96
30	m^*	10	Bagno and Scorrano	NMR chemical shift of free base and protonated base	97
31	NCo	25	Waris	ratio of fluorescence intensities of bands I and III of vibronic spectra of naphtha[2,3-α]coronene	78
32	Ov	25	Waris	relative band intensities (I/III) for ovalene fluorescence spectra	80
33	pK_{BH^+}	10	Bagno and Scorrano	NMR chemical shift of free base and protonated base	97
34	P_s	108	Middleton	bathochromic UV-vis spectra shifts of λ_{max} of (α-perfluoroheptyl-β,β-dicyanovinyl)aminostyrenes	98
35	P_y	94	Dong and Winnik	relative band intensities I_1/I_3 for pyrene fluorescence spectra	99
36	Q_f	12	Abdel-Mottaleb	fluorescence properties of 7-hydroxy-4-methylcoumarin laser dye	100
37	Qm	52	Marvel	heat of mixture of chloroform with solvents by infrared spectra	101
38	SA	121	Catalán and Díaz	solvent acidity, evaluated from UV-vis spectra of *o*-*tert*-butylstilbazolium betaine dye and its nonbasic homomorph *o*,*o*′-di-*tert*-butylstilbazolium betaine dye	102

Table 1 (Continued)

no.	scale[a]	no. of solvents[b]	author(s)[c]	physical background	refs[d]
				Spectroscopic Measurements (Continued)	
39	SB	202	Catalán	solvent basicity, evaluated from UV-vis spectra of 5-nitroindoline and its nonacid homomorph 1-Me-5-nitroindoline	57
40	SPP SPP$^{\mathrm{N}}$	100	Catalán	calculated from UV-vis spectra of 2-(dimethylamino)-7-nitrofluorene and its homomorph 2-fluoro-7-nitrofluorene	48
41	T_{ex}	6	Fujita	hydroxyl proton exchange time at 30 °C	103
42	XX	19	David and Hallam	solvent-induced frequency shifts of SO_2	104
43	Z	31	Marcus	transition energies for charge-transfer band of complex from 1-ethyl-4-methoxycarbonylpyridinium iodide	14
44	α	185	Marcus	solvatochromic parameter of solvent HBD (hydrogen-bond donor) acidity	14
45	β	185	Marcus	solvatochromic parameter of solvent HBA (hydrogen-bond acceptor) basicity	14
46	π^*	229	Laurence	solvatochromic parameter: index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect	47
47	π^*_{aso}	29	Buncel and Rajagopal	bathochromic shifts of six azo merocyanine dyes	49
48	χ_{R}	58	Brooker	transition energy of merocyanine dye (VII)	105
49	$\int^{\mathrm{C_6H_5F}}$	24	Taft	^{19}F NMR shielding parameters of fluorobenzene in infinitely dilute solutions relative to fixed external standard (20% *p*-difluorobenzene in CCl_4)	106
50	$\int_{\mathrm{H}}^{\mathrm{P-NO_2}}$	29	Taft	^{19}F NMR shielding parameters in *p*-nitrofluorobenzenes	107
51	$\int_{\mathrm{N}}^{\mathrm{pyrrole}}$	13	Witanowski	nitrogen NMR shieldings of pyrrole referred to neat nitromethane	108
52	$\delta_{\mathrm{Li^+}}$	11	Popov	chemical shifts of Li nucleus in different solvents	109
53	Δ	55	Gurka and Taft	difference of ^{19}F nucleus shifts of *p*-fluorophenol between that in solvents and that in carbon tetrachloride	110
54	δ_0	15	Bloor and Kidd	^{23}Na chemical shifts of sodium iodide in different solvents	111
55	$\Delta_{\mathrm{1-Et}}$	23	Anderson and Symons	internal shift of 1-ethyl group of 1,4-diethylpyridinium	112
56	ΔR	36	Anderson and Symons	difference between the 2,6- and 3,5-ring proton shift of 1,4-diethylpyridinium	112
57	$\Delta\delta_{\mathrm{CHCl_3}}$	28	Hahn	shift of pure chloroform relative to that of chloroform in dilute solution	113
58	$\Delta\upsilon_{\mathrm{A}}$	30	Kagiya	perturbation of solvents on the C═O vibration band of acetophenone	53
59	$\Delta\upsilon_{\mathrm{D}}$	92	Kagiya	perturbation of solvents on O−D vibration band of methanol-*d*	53
60	θ_{1K}	80	Sjöström and Wold	polarity of solvent, based on PCA combined with a cross-validation technique of solvatochromic shift data	114
61	θ_{2K}	80	Sjöström and Wold	polarizabiliy of solvent, based on PCA combined with a cross-validation technique of solvatochromic shift data	114
62	λ	24	Thomas	maximum absorption of electronic spectra of heteroleptic molybdenum complexes	115
63	$\lambda_{\mathrm{A}}^{\mathrm{MNPS}}$	6	Raileanu	absorption maxima for MNPS	116
64	$\lambda_{\mathrm{A}}^{\mathrm{MS}}$	14	Catalán	absorption band maxima for MS	117
65	$\lambda_{\mathrm{A}}^{\mathrm{Na}}$	7	Toma and Takasugi	maximum absorption wavenumbers for charge-transfer bands of $Na_3(acpy)Fe(CN)_5$	118
66	$\lambda_{\mathrm{F}}^{\mathrm{MHN12}}$	21	Catalán	fluorescence band maxima for MHN12	117
67	π_1^*	96	Abe	calculated from the frequency shifts of the electronic absorption spectra of *N*,*N*-dimethyl-4-nitroaniline	51
68	π_2^*	72	Abe	calculated from the frequency shifts of the electronic absorption spectra of naphthalene	51
69	π_{AV}	19	Taft	aromatic ^{13}C NMR shifts induced by protonic solvents in a solution of benzotrifluoride and phenylsulfurpentafluoride	119
70	τ	9	Sukowski	vibrational cooling times of azulene by ps spectra study	120
71	$\upsilon_{\mathrm{a}}-\upsilon_{\mathrm{m}}$	12	Werner and Rodgers	Stoke shift of fluorescence spectrum of *N*,*N*-diethyl-9-anthramide	121
72	υ^{C}	32	Catalán	wavenumber of first UV-vis absorption maximum of chromophore $Me_2NT_2NO_2$	122
73	υ_{CE}	22	Lark	relative infrared frequency shifts for chloroethane	123
74	$\Phi_{\mathrm{f}}^{\mathrm{BBVB}}$		El-Daly	fluorescence quantum yield of BBVB	124
75	$\varphi_{\mathrm{f}}^{\mathrm{CEA}}$	8	Saito	fluorescence quantum yield of coelenteramide	125
76	χ_{B}	12	Brooker	transition energy of merocyanine dye (IV)	105
77	ϵ_{s}	16	Fox and Hayon	static dielectric constant	83
78	$\Delta\nu_{\mathrm{CI}}$	68	Laurence	IR frequency shifts of iodine cyanide C−I bonds	126
79	$\Delta\nu_{\mathrm{OH}}$	68	Laurence	IR frequency shifts of phenol hydroxyl group	126
80	$\epsilon^{-}{}_{\sigma o\lambda}$	16	Fox and Hayon	absorption maxima of solvated electrons	83
				Equilibrium Measurements	
81	C_{B}	123	Drago	susceptibility to covalent interaction of a base statistical from ΔH data of different bases and acids	127
82	D1	18	Eliel and Hofer	$\Delta G°$ between *cis*- and *trans*-2-isopropyl-5-methoxy-1,3-dioxane	128
83	D_{H}	24	Persson	ΔG of transfer of Na^+ from solvent to reference solvent (1,2-dichloroethane) for hard acceptors	38
84	DN	66	Marcus	donor number, negative ΔH value for 1:1 adduct formation between $SbCl_5$ and solvent molecules in dilute solution of 1,2-dichloroethane	14
85	$E_{\mathrm{(H-bond)}}$	13	Banerjee	calculated $E_{\mathrm{(H-bond)}}$ values from the enthalpies of solvent for seven solute-solvent systems	129

Table 1 (Continued)

no.	scale[a]	no. of solvents[b]	author(s)[c]	physical background	refs[d]
Equilibrium Measurements (Continued)					
86	$E_{1/2}^{\mathrm{U}}$	9	Seeber and Zanello	formal electrode potentials for the couple $\mathrm{U^{IV}-U^{V}}$ in different solvents	130
87	E_{BB}	123	Drago	susceptibility to electrostatic interaction of a base statistical from ΔH data of different bases and acids	127
88	E_{enzyme}	9	Fitzpatrick and Klibanov	enantioselectivity of subtilisin Carlsberg in transesterification reaction between the chiral alcohol *sec*-phenethyl alcohol and the ester vinylbutyrate	131
89	$\mathrm{HCl_{sol}}$	21	Gerrard	solubility of hydrogen chloride in solvents	132
90	$\log K_{\mathrm{f}}$	6	Rounaghi and Popov	stability constants of sodium complexes with DITHIA-18C6	133
91	$\mathrm{Log}\ K\mathrm{s}^{\mathrm{Na-L}}$	10	Lada	stability constants of Na and dibenzo-18-crown-6 complex in different solvents	134
92	PA	20	Long and Munseon	calculated from equilibrium constants for various gaseous proton-transfer reactions with various solvents	135
93	Sp	13	Abraham	solvophobic parameter, calculated from the energies of solute transfer from water to solvents	136
94	$S_{\mathrm{p,enzyme}}$	17	Terradas	prochiral selectivity of *Pseudomonas* sp. lipase in hydrolysis	137
95	$S_{\mathrm{S,\ enzyme}}$	20	Wescott and Klibanov	substrate specificity of the serine protease subtilisin Carlsberg in the transesterification reaction of N-Ac-L-Ser-OEt and N-Ac-L-Phe-OEt with 1-propanol	138
96	X	28	Fletcher	absorption of solution	139
97	$\Delta_{\mathrm{acid}}H$	63	Catalán	calculated by measuring the difference between the solvation enthalpies of *N*-methylimidazole and *N*-methylpyrrole along with SPP scale values	140
98	$\Delta G^{\mathrm{t}}_{\mathrm{w\rightarrow s}}$	12	Ugo	voltammetry determined free energies of proton transfer from water to solvent	141
99	$\Delta G_{\mathrm{t}}{}^{0}{}_{\mathrm{(TPA)}}$	10	Treiner	experimental single tetraphenylarsenium ion standard free energy of transfer from water to organic solvents	142
100	ΔH_{MIm}	22	Bustamante and Drago	experimental values of enthalpies of MIm−solvent system	143
101	ΔH_{PS}	8	Benoit and Figeys	calorimeter-determined enthalpies of solution of 1,8-bis(dimethylamino)naphthalene in different solvents	144
102	ΔH_{v}	22	Wilhelm and Battino	experimental enthalpy of vaporization	145
103	$\Delta S_{\mathrm{S}}°$	9	Sen	experimental values of entropy of solvation of electrolyte NaBr	146
104	$\Delta H°_{\mathrm{solv}}$	36	Catalán	linear combination of the $\Delta H°_{\mathrm{solv}}$ for the four probes (pyrrole, *N*-methylpyrrole, benzene, and toluene)	147
105	ε^{0}	31	Robinson	average equilibrium and chromatographic distribution constants on Amberlite XAD-2, SM-2, and XAD-4	148
106	Ω	36	Berson	endo/exo/ product ratio for the cyclopentadiene−methyl acrylate Diels-Alder addition at 30 °C	149
107	$-\Delta H^{0}{}_{\mathrm{BF_3}}$	76	Maria and Gal	enthalpy of complexation of solvents with $\mathrm{BF_3}$ in dichloromethane	30
108	μ_{M}	34	Marcus	difference between mean of the Gibbs free energies of transfer of sodium and potassium ions from water to a given solvent and the corresponding quantity for silver ions divided by 100	27
Kinetic Measurements					
109	$\mathrm{BINAP}-\tau_{\mathrm{iso}}$	15	Bowman and Eisenthal	isomerization times of 1,1′-binaphthyl	150
110	$\mathrm{BINAP}-\tau_{\mathrm{or}}$	15	Bowman and Eisenthal	reorientation times of 1,1′-binaphthyl	150
111	D_{π}	34	Oshima	second-order rate constant of the reaction of DDM and TCNE	151
112	$K_{\mathrm{4-nitro-deaab}}$	10	Marcandalli	kinetic constants of cis−trans isomerization reaction of 4-nitro-4-diethylaminoazobenzene	152
113	K_{DC}	24	Kemp and Paul	rate constants for decarboxylation of 3-carboxybenzisoxazoles	153
114	$K_{\mathrm{ET}}^{\mathrm{Co}}$	9	Pyati and Murray	electron-transfer rates for the redox couple $[\mathrm{Co(bpy)_3}]^{2+/3+}$	154
115	K_{ion}	11	Smith	first-order rate constant of the ionization of *p*-methoxyneophyl-*p*-toluenesulfonate	155
116	$K_{\mathrm{PhNH_2/BO}}$	14	MacFaul	measured rate constants for the hydrogen abstraction reactions from aniline by *tert*-butoxyl radicals	156
117	Kq	27	Aubry	bimolecular rate constants of single oxygen quenching	157
118	K_{r}	10	Harano	first-order rate constant for rearrangement of *o*-(1-cyclopropylethyl) *S*-methyl dithiocarbanate	158
119	$\mathrm{Log}(K)_{\mathrm{EDBT}}$	5	Kevill and Anderson	first-rate constants of solvolysis of *S*-ethyldienzothiophenium	159
120	N_{BS}	12	Bentley	rate constant for solvolysis of $\mathrm{CH_3OTs}$ in solvent of ionizing power Y relative to rate constant for solvolysis in 80% ethanol	160
121	N_{T}	6	Kevill and Anderson	specific rates of solvolysis of *S*-methyldibenzothiophenium ion	161
122	Rp	20	Pincock	rate constants of pyridine-catalyzed decomposition of *tert*-butylperoxy formate in various solvents at 90 °C	162
123	Y^{+}	6	Kevill and Anderson	first rate constants for the solvolysis of 1-adamantyl-dimethylsulfonium trifluoromethanesulfonate	163
124	$Y_{\mathrm{1-OTr}}$	5	Takeuchi	rate constants of solvolysis of 1-adamantyl tresylate	164
125	$Y_{\mathrm{2-OTr}}$	5	Takeuchi	rate constants of solvolysis of 2-adamantyl tresylate	164
126	Y_{Br}	5	Bentley	rate constants of solvolysis of 1-adamantyl bromide	165
127	Y_{Cl}	5	Bentley	rate constants of solvolysis of 1-adamantyl chloride	165

Table 1 (Continued)

no.	scale[a]	no. of solvents[b]	author(s)[c]	physical background	refs[d]
				Kinetic Measurements (Continued)	
128	Y_I	5	Bentley	rate constants of solvolysis of 1-adamantyl iodide	166
129	Y_{OTf}	8	Creary and McDonald	first rate constants for solvolysis of 7-norbornyl triflate	167
130	$Y_{OTf}{}^{K}$	5	Kevill and Anderson	first rate constants for solvolysis of 2-adamantyl trifluoromethanesulfonate	168
131	χ^-	8	Mitsuhashi	calculated from kinetic data of anion solvation	169
132	χ^+	8	Mitsuhasi	calculated from kinetic data of cation solvation	169
				Other Measurements	
133	A	55	Swain	anion solvating tendency	24
134	$a_1{}^{298}$	26	Wilhelm	effective hard sphere diameter	170
135	Ap	18	Fawcett	calculated from data for Gibbs solvation energy for alkali metal cations and halide ions	171
136	BB*	55	Swain	cation solvating tendency	24
137	Bp	18	Fawcett	calculated from data for Gibbs solvation energy for alkali metal cations and halide ions	171
138	C	28	Cilli	swelling degree of resin (%)	172
139	d	57	Fowler and Katritzky	dielectric constant	8
140	DC	22	Khmelnitsky	calculated from thermodynamic model of protein denaturation	173
141	E	84	Koppel and Palm	acidity derived from E_T and P and Y	9
142	Ed	7	Matyushov and Schmid	calculated value for energy of solvent reorganization of density for $(bpy)_2ClRu(4,4'\text{-}bpy)RuCl(bpy)_2{}^{3+}$	174
143	E^k	20	Koppel and Palm	derived from Dimroth's E_T polarity parameter by subtracting the contribution of nonspecific solvation	77
144	E_m	5	Morrone	calculated from degree of conversion and ee of the transesterification product	175
145	Ep	7	Matyushov and Schmid	calculated value for energy of solvent reorganization of dipoles for $(bpy)_2ClRu(4,4'\text{-}bpy)RuCl(bpy)_2{}^{3+}$	174
146	ES	14	Colin	eluotropic strength of solvents to different compounds	176
147	$-E_s'$	17	Palm	subtract an arbitrary constant 0.25 from the corrected values of Taft's substituent parameters	77
148	J	57	Fowler and Katritzky	expression of dielectric constant	8
149	$K_s{}^{Li^+}$	10	Filipek	based on polarographic study of Tl^-, Li^-, Na^-, K^-, and Cs^- complexes with monensin anion	177
150	Log K	27	Leggett	solvatochromic parameter α calculated from other solvent scales	178
151	Log L^{16}	168	Abraham	based on logarithmic gas−liquid partition coefficient in *n*-hexadecane	179
152	Log P	107	Laane	partition coefficient, calculated from hydrophobic fragmental constants	180
153	M	57	Fowler and Katritzky	expression of refractive index	8
154	N	57	Fowler and Katritzky	dielectric function	8
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156	P'	78	Snyder	chromatography strength	181
157	PK_a'	8	Barrette	effective acidity for Brønsted acid−phenol in aprotic solvents by voltammetry test at a platinum electrode	182
158	q^-	29	Famini and Wilson	electrostatic HBAB	183
159	q^+	29	Famini and Wilson	electrostatic HBDA	183
160	Q_{Si}	7	Lauerhaas	luminescence quenching ratio of porous Si in solvents to their gas-phase dipole moment	184
161	S	48	Brownstein	derived from Kosower's Z values, uses R for process sensitivity	185
162	S'	46	Drago	solvent polarity, derived from experimental observations $\Delta\chi = PS' + W$	61
163	V_{mc}	30	Famini and Wilson	molecular volume	183
164	Xd^R	52	Rutan	selectivity parameter: reflects a composite of solvent dipolarity-polarizability, hydrogen bond basicity, and hydrogen bond acidity	186
165	Xe^R	52	Rutan	selectivity parameter: reflects a composite of solvent dipolarity and solvent acidity	186
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167	X_d	72	Snyder	proton donor index	181
168	X_e	72	Snyder	proton acceptor index	181
169	X_n	72	Snyder	strong dipole	181
170	Y	42	Koppel and Palm	polarity expression of dielectric constant	9
171	δ	29	Hildebrand	square root of cohesive energy density	187
172	ΔE^{R-P}	5	Jensen and Parker	redox potential of perylene	188
173	$\Delta G_{6Å}$	25	Neumann	calculated energy necessary to form a cavity of appropriate size for solute of 6 Å diameter from effective hard-sphere diameter of solvent	189
174	ΔH^{acid}	36	Catalán	calculated from enthalpies of solution of two probes, *N*-methylimidazole and *N*-methylpyrrole, and relative permittivity	190
175	$-\Delta H_f$	27	Arnett	heat of formation for the hydrogen bond	191
		56	Demyanovich and Lynn		192
176	$\varepsilon^0{}_{alumina}$	23	Park and Carr	calculated from other solvent parameters π^*, α, and β	193
177	$\varepsilon^0{}_{silica}$	19	Park and Carr	calculated from other solvent parameters π^*, α, and β	193
178	ε_A	30	Famini and Wilson	covalent HBDA	183
179	ε_B	29	Famini and Wilson	covalent HBAB	183

Table 1 (Continued)

no.	scale[a]	no. of solvents[b]	author(s)[c]	physical background	refs[d]
			Other Measurements (Continued)		
180	$\Theta(\in_B)$	29	Abboud and Taft	expression of dielectric constants	194
181	μ_D	39	Abboud and Taft	dipole moments	194
182	π_I	30	Famini and Wilson	polarizability index	183
183	σ_1	25	Neumann	calculated from surface tension of hard sphere liquid	189
184	γ_{SO_2}	17	Demyanovich and Lynn	experimental infinite dilution activity coefficients of SO_2	192

[a] In alphabetical order for Latin and Greek, respectively. [b] Some numbers given in this column are arbitrary. Sometimes authors did not number the values, similar measurements were made in different conditions, etc. [c] Main authors only. [d] References given in this column are not original references. We tried to choose the references that contained more experimental data. [e,f,g] To avoid duplication, we renamed B, X, and E_B scales to B-2, XX, and E_{BB}, respectively.

Koppel and Palm,[17] Kamlet and Taft,[18-20] Krygowski and Fawcett,[21-23] Swain,[24] Mayer,[25] Dougherty,[26] etc.

Empirical properties used to define solvent polarity scales include the following general classes: (i) equilibrium and kinetic rate constants of chemical reactions, (ii) spectroscopic and other properties of solvents, (iii) spectroscopic and other properties of solutes, and (iv) multiparameter approaches.

2.2. Types of Properties Used To Define Solvent Polarity Scales: Division into Major Classes and Definitions

The different types of physicochemical properties used to define solvent polarity scales are now considered.

2.2.1. Equilibrium and Kinetic Measurements

The influence of solvent on chemical equilibria is determined by the standard molar Gibbs energy of solute (reagent) transfer from one solvent to another or standard molar Gibbs energy of solvation of reagents. Thermodynamically, the standard molar Gibbs energy, $\Delta G°$ consists of two components, the enthalpy $\Delta H°$ and the entropy term $T\Delta S°$, respectively. Consequently, the corresponding enthalpy and entropy functions can be defined also for the solute transfer and solvation. Advances in calorimetry have made standard molar transfer enthalpies readily available. If transfer Gibbs energies and transfer enthalpies are both available, a complete dissection of the effect of the solvents on the various thermodynamic parameters should be possible.

The overall solvent effect on a chemical equilibrium constant is determined by the solvation (transfer) free energies of participating reagents and products of the reaction. The contributions from different microscopic interactions (electrostatic, dispersion, hydrogen bonding, etc.) to the transfer free energy of each solute can vary. Therefore, a quantitative description of solvent effects on equilibria proceeding solely from the equilibrium constants of a certain standard reaction would be possible only in simple and favorable cases.[3]

The same is valid for the use of rate constants and the related free energies of activation of chemical reactions. In each case, apart from the transfer free energies of reagents, the solvation of the transition state of the reaction has to be accounted for.

Nevertheless, changes in rate and in equilibrium constants occurring in one reaction series have been often related to those in another related series. Thus, plotting the logarithms of rate or equilibrium constants for one reaction series against the corresponding constants for a second, related series frequently gives a straight line. Consequently, the linear expression of Gibbs energy relationships in terms of ratios of constants by referring all members of a reaction series to a reference member of the series has been used both in the study of reaction mechanism and in the prediction of reaction rates or equilibrium constants dependent on substituent or solvent changes.[3]

2.2.1.1. Scales Based on Measurements of Equilibria and Kinetics. *A.* The μ_M scale was developed by Marcus[27] for determining the "softness" of the solvent. The basic hypotheses and physical meaning concern the standard molar Gibbs energies of transfer $\Delta_t G°(W \rightarrow S)$ of ions from a reference solvent (water, W) to other solvents (S). The factor $\Delta_t G°(W \rightarrow S)$ should reflect the softness of these solvents in a different manner for hard or soft ions. Other things being equal, especially the charge and size of the ions, hard ions should prefer water and soft ions the softer solvents. Marcus compared the value of $\Delta_t G°(W \rightarrow S)$ for Ag^+ (considered to be the softest univalent ion) with the mean of $\Delta_t G°(W \rightarrow S)$ values for Na^+ and K^+. Then results form the basis of the softness scale μ_M, defined as

$$\mu_M = \{[1/2][\Delta_t G°(Na^+, W \rightarrow S) + \Delta_t G°(K^+, W \rightarrow S)] - \Delta_t G°(Ag^+, W \rightarrow S)\}/100 \quad (2)$$

The sign of the expression is chosen so as to make μ_M more positive the softer the solvent S. The division by 100 [for values of $\Delta_t G°(W \rightarrow S)$ expressed in kJ/mol] serves to bring the values of μ_M to a magnitude similar to other solvent property indices used in linear solvation energy relationships, that is, approximately between 0 and 1.[27]

B. The SP, softness parameter for a solvent S, was defined by Gritzner[28] in 1988 on the basis of eq 3:

$$SP(S) = 25 + |\Delta_t G°(BCN \rightarrow S)| \quad (3)$$

$|\Delta_t G°(BCN \rightarrow S)|$ is the absolute value of the standard Gibbs energy change pertaining to the transfer of Ag^+ from benzonitrile to solvent S. The addition of 25 kJ/mol and the use of the absolute value of $|\Delta_t G°(BCN \rightarrow S)|$ are designed to make all values positive. A study published in 1993[29] reported additional $|\Delta_t G°(\mathrm{BCN}\rightarrow\mathrm{S})|$ values.

The physical meaning of SP is that this parameter is essentially a measure of the interactions between soft acceptor solutes and soft solvents. In principle, the SP scale also contains contributions from a purely electrostatic interaction between Ag^+ and the solvent.

C. DN and $\Delta H°_{BF_3}$. The "donicity number" (DN) was developed in 1966 by Gutmann.[10] It is defined operationally as the negative of the standard enthalpy changes, $\Delta H°_{\mathrm{SbCl_5}}$ for the formation of the 1:1 adduct between antimony pentachloride and an electron pair donor solvent D, both in dilute solution in 1,2-dichloroethane at 25.0 °C and 0.1 MPa:

$$\mathrm{D\ (soln) + SbCl_5\ (soln) \leftrightarrow D{:}SbCl_5\ (soln)} \quad (4)$$

$\Delta H°_{\mathrm{SbCl_5}}$ is given by eq 5

$$\Delta H°_{\mathrm{SbCl_5}} = \Delta H_1 - \Delta H_2 \quad (5)$$

where ΔH_1 and ΔH_2 are the enthalpy changes under standard conditions for the following reactions:

$$\mathrm{D\ (pure\ liquid) + SbCl_5\ (soln) \leftrightarrow D{:}SbCl_5\ (soln)} \quad (6a)$$

and

$$\mathrm{D\ (pure\ liquid) \leftrightarrow D\ (soln)} \quad (6b)$$

The DN scale has been used particularly in the field of coordination chemistry. Maria and Gal[30] have published a very careful critical compilation of the available DN values. Very important also are the results presented by Olofsson and co-workers.[31]

Maria and Gal[30] defined the scale $\Delta H°_{\mathrm{BF_3}}$ as the standard enthalpy change for the reaction of the formation of the 1:1 adduct between boron trifluoride and electron pair donor solvents D, both in dilute solution in dichloromethane at 25.0 °C and 0.1 MPa:

$$\mathrm{D\ (soln) + BF_3\ (soln) \leftrightarrow D{:}BF_3\ (soln)} \quad (7)$$

The $\Delta H°_{\mathrm{BF_3}}$ values seem to be less affected by the same problems as the DN numbers (reactions of basic impurities, major anomalies for pyridine, triethylamine, hexamethylphosphoric triamide, and HMPA).

The basic hypothesis involved in the use of these scales is the assumption that the quantitative ranking of "donicity" they define also holds for the same compounds acting as solvents.

2.2.2. Spectroscopic Measurements

Spectroscopic definitions of solvent polarity have been derived from solvent-sensitive standard compounds absorbing radiation in the UV-vis, IR, ESR, and NMR spectral ranges. Theories of solvent effects on absorption spectra assume the isolated and solvated chromophore-containing molecules to be distinct chemical identities and treat these effects simply as a physical perturbation of the relevant molecular states of the chromophores. Onsager's model of dielectrics[32] has been generally used for the theoretical explanation of solvent shifts, even when the theory was derived as a quantum mechanical treatment, that is, the theory of McRae, which relates solvent-induced frequency shifts to electric dipole interactions.[33]

According to Reichardt,[3] "The term solvatochromism is used to describe the pronounced change in position (and sometimes intensity) of an UV/VIS absorption band, accompanying a change in the polarity of the medium ...". A hypsochromic (or blue) shift, with increasing solvent polarity, is usually called *negative solvatochromism*. The corresponding bathochromic (or red) shift is termed *positive solvatochromism*.

The suggestion that solvatochromic dyes should be used as indicators of solvent polarity was first made by Brooker et al.[34] in 1951. Bayliss and McRae noticed in 1954 that the solvent effects in electronic absorption spectra are to be expected from (i) the presence of a dipole moment in the solute or solvent molecule, (ii) the change in dipole moment during the optical transition, and (iii) the operation of the Franck-Condon principle.[35] They studied solution spectral data for acetone, crotonaldehyde, nitromethane, and nitrobenzene to illustrate these principles.[36] Kosower[5] in 1958 set up the first comprehensive solvent scale.

The most important solvent polarity scales developed using empirical parameters from spectroscopic measurements include the following.

2.2.2.1. "Solvation" Scales Derived from Spectroscopic Measurements. *A.* $E_T(30)$ and E_T^{N} [3] are defined as the molar transition energy, in kcal/mol, for the long wavelength electronic transition of a 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate dye (Dimroth-Reichardt's betaine dye) as a solution in the solvent under investigation at 25 °C and at a pressure of 0.1 MPa. The $E_T(30)$ values are obtained from the experimentally determined wavelength of the absorption maximum of this transition ($\lambda_{\max}$) through eq 8:

$$E_T(30)/(\mathrm{kcal/mol}) = 28591/(\lambda_{\max}/\mathrm{nm}) \quad (8)$$

E_T^{N} is a dimensionless "normalized" scale, defined by eq 9, wherein tetramethylsilane (TMS) and water are selected as the "polarity" extreme cases.

$$E_T^{\mathrm{N}}\ (\mathrm{solvent}) = [E_T(\mathrm{solvent}) - E_T(\mathrm{TMS})]/[E_T(\mathrm{water}) - E_T(\mathrm{TMS})] \quad (9)$$

B. Z [37] is based on the high solvent-sensitivity of the frequency of the charge-transfer absorption band of the indicator 1-ethyl-4-methoxycarbonylpyridinium iodide. Kosower defined his polarity parameter for a given solvent as the molar transition energy, in kcal/mol, for the long-wavelength electronic transition of 1-ethyl-4-methoxycarbonylpyridinium iodide, dissolved in the solvent under consideration at 25 °C and at a pressure of 0.1 MPa. Values of Z are obtained through an expression similar to eq 8, from the experimentally determined wavelength of the absorption maximum of this transition ($\lambda_{\max}$).

C. Z^t [14] is the symbol proposed by Marcus to be used for the scale of medium effects based on the solvatochromic shifts undergone by the longest wavelength band in the electronic absorption spectrum of

4-cyano-1-ethylpyridinium iodide. Medium effects on the corresponding transition energies are linearly related to *Z* values to a very high degree of correlation and a standard deviation of 0.5 kcal/mol.

D. The D_s scale was defined by Persson, Sandström, and Goggin[38] in 1986, based on the shifts undergone by the position of the symmetric Hg−Br stretching vibration in mercuric dibromide, $HgBr_2$, on going from the gas phase to the solvent (eq 10). The σ values were determined at 25.0 °C by Raman spectroscopy; the uncertainties in σ are estimated as $\cong 1$ cm^{-1}.[38]

$$D_s = \sigma_{Hg-Br(gas)} - \sigma_{Hg-Br(solvent)} \qquad (10)$$

E. *G* is the scale developed by Schleyer and Allerhand[39] on the basis of a quantitative study of the solvent shifts undergone by the positions of the stretching vibrations, σ, of selected X = O oscillators. The authors defined the *G* scale through eq 11, wherein σ^O and σ^S, respectively, stand for the positions of the stretching vibration of X = O in the gas phase and in solvent S, and *a* is a constant characteristic of the probe. In the development of the scale, these authors used the carbonyl stretching bands of *N*,*N*-dimethylformamide and benzophenone[40] and the SO stretch of DMSO.[41] In 1986, Somolinos, García, and others[42] revised and extended the *G* scale, also at 0.1 MPa and "room temperature".

$$aG = (\sigma^O - \sigma^S)/\sigma^O \qquad (11)$$

Later, Nicolet, Laurence, and Luçon[43] studied in 1987 the solvent shifts undergone by the C═O stretching band of methyl trichloroacetate. It became obvious that this band has several features that make it particularly suitable as a molecular probe.

Finally, Kolling measured the position of the carbonyl stretching vibration of ethyl acetate[44] and butanone[45] in a variety of solvents at 298.15 K and 0.1 MPa.

2.2.2.2. Scales of Dipolarity/Polarizability Based on Spectroscopic Measurements. The basic concept of these scales is that the solute-solvent interactions can be dissected into "general"—which have electrostatic and dispersive origins and can be related conceptually to reaction field theories—and "specific" interactions—which include hydrogen-bonding and/or donor-acceptor interactions.[3]

A. π^* was defined by Kamlet, Abboud, and Taft[18] and intended to provide a quantitative measure of the nonspecific part of van der Waals interactions between solvents and solutes. The scale was based on the treatment of the solvatochromic shifts undergone by selected absorption bands of a variety of aromatic molecules ("molecular probes"). Given a solvatochromic indicator, the π^* value for a solvent S was defined through eq 12. σ(S) pertains to the frequencies of the maximum of the solvatochromic band in the various solvents. Cyclohexane ($c\text{-}C_6H_{12}$) and dimethyl sulfoxide (DMSO) were used as references by defining $\pi^*(c\text{-}C_6H_{12}) = 0$ and $\pi^*(DMSO) = 1$.

$$\pi^*(S) = [\sigma(S) - \sigma(c\text{-}C_6H_{12})]/[\sigma(DMSO) - \sigma(c\text{-}C_6H_{12})] \qquad (12)$$

In 1986, Laurence and Nicolet,[46] after careful examination of the original conditions (temperature, medium effects, etc.) used for the construction of the π^* scale, concluded that (i) the solvatochromic band of the most used indicator, *p*-(diethylamino)nitrobenzene, has significant vibrational structure, leading to a solvent-dependent band shape; (ii) π^* values are somewhat solute-dependent; and (iii) for a given indicator, π^* values are temperature-dependent ("thermosolvatochromism").

M. T. Dalati[47] reported in 1991 the frequencies of the solvatochromic bands of *p*-methoxynitrobenzene and *p*-(dimethylamino)nitrobenzene in 276 solvents at 25.0 °C and 0.1 MPa. The corresponding π^* values were obtained for each of these two indicators (π^*_{NMe2} and π^*_{OMe}) by means of eq 12 and the conditions $\pi^*(c\text{-}C_6H_{12}) = 0$ and $\pi^*(DMSO) = 1$. An analysis of these π^*, π^*_{NMe2}, and π^*_{OMe} values demonstrated that they are generally interrelated but can show significant quantitative differences.

B. SPP (solvent polarity-polarizability), reported by Catalán et al.,[48] is based on the solvatochromic shifts undergone by the long-wavelength absorption maximum of two indicators: 2-(dimethylamino)-7-nitrofluorene (DMANF) and 2-fluoro-7-nitrofluorene (FNF). For a given solvent S, the value of this parameter is defined through eq 13:

$$SPP(S) = [\Delta\sigma(S) - \Delta\sigma(c\text{-}C_6H_{12})]/[\Delta\sigma(DMSO) - \Delta\sigma(c\text{-}C_6H_{12})] \qquad (13)$$

Catalán *et al.*[48] proposed a scale with a different normalization (SPP^N) wherein the origin is not $\Delta\sigma(c\text{-}C_6H_{12})$ but rather the calculated value of $\Delta\sigma$(gas).

C. π^*_{azo} scales based on the solvatochromic shifts undergone by the longest wavelength absorption band ($n \rightarrow p^*$ and $\pi \rightarrow p^*$ transitions) of a set of six azo merocyanine dyes were reported by Buncel and Rajagopal.[49] Studies were made of the spectra of the six indicators in 29 different solvents (25 of which were either non-hydrogen-bond donors or weak-hydrogen-bond donors). The frequencies of the maxima were determined at 25 °C and under 0.1 MPa. Buncel and Rajagopal could thus demonstrate that the qualities of the correlations of medium effects on solute properties obtained using π^* or π^*_{azo} are very close, indicating that these scales all keep only little "model-dependent" specificity.[50]

D. π^*_2 is a scale developed by Abe[51] based on the solvatochromic shifts undergone by the long-wavelength electronic absorption transitions of three indicators: naphthalene, anthracene, and β-carotene. The scale was normalized by taking $\pi^*_2 = 0$ for the gas phase and $\pi^*_2 = 1$ for $c\text{-}C_6H_{12}$ solvent. For any given solvent S, π^*_2 (S) was given by eq 14. Abe observed that solvent effects on the frequency of the electronic transition of anthracene are linearly related to a high degree of precision. This correlation was used to generate π^*_2 values for solvents for which no naphthalene data were available.

$$\pi^*_2\,(\mathrm{S}) = [\sigma(\mathrm{S}) - \sigma(\mathrm{gas})]/[\sigma(\mathrm{c\text{-}C_6H_{12}}) - \sigma(\mathrm{gas})] \quad (14)$$

2.2.2.3. Basicity Scales. These scales quantify the "specific" solute-solvent interactions in which the solute plays the role of an electron pair acceptor and the solvent, an electron pair donor. Here we discuss only some frequently used scales of hydrogen bonding and basicities of solvents.

A. $\Delta\nu_{OD}$ ($\Delta\sigma_{OD}$) and B Scale. In 1940, Stanford and Gordy[52] used the sensitivity of the O−H (or O−D) oscillators to hydrogen bonding as a tool to quantify the Lewis basicity of molecules. Kagiya, Sumida, and Inoue[53] determined the positions ($\mathrm{cm^{-1}}$) of the O−D stretching band of monomeric methanol [^{2}H] in different solvents and took the difference between the positions of the absorption maximum in solvent S and in benzene, $\Delta\sigma_{\mathrm{OD}} = \sigma(\mathrm{S}) - \sigma(\mathrm{C_6H_6})$, as a quantitative measure of the HBA character of these solvents. In 1976, Burden, Collier, and Shorter[54] revised and extended this study.

Koppel and Palm[9] defined a scale of Lewis basicity of solvents, *B*, through eq 15, wherein $\sigma_{\mathrm{OD}}(\mathrm{gas})$ and $\sigma_{\mathrm{OD}}(\mathrm{S})$ stand for the values of σ_{OD} in the gas phase and in solvent S.

$$B = \sigma_{\mathrm{OD}}(\mathrm{gas}) - \sigma_{\mathrm{OD}}(\mathrm{S}) \quad (15)$$

B. The *B′* scale was developed by Koppel and Paju[55] by redefining the scale *B* of solvent Lewis basicity through eq 16

$$B' = \Delta\sigma_{\mathrm{PhOH}}{}^{\mathrm{CCl_4}} = \sigma_{\mathrm{PhOH}}{}^{\mathrm{CCl_4}} - \sigma_{\mathrm{PhOH-S}}{}^{\mathrm{CCl_4}} \quad (16)$$

wherein $\sigma_{\mathrm{PhOH}}{}^{\mathrm{CCl_4}}$ stands for the position (in $\mathrm{cm^{-1}}$) of the O−H stretching mode of monomeric phenol in tetrachloromethane solution and $\sigma_{\mathrm{PhOH-S}}{}^{\mathrm{CCl_4}}$ is the position of the O−H stretching mode of phenol within the 1:1 complex with molecule S in tetrachloromethane solution. According to Koppel and Paju,[55] "... the representation of the solvent basicity parameters by eq 16 is equivalent to the introduction of the postulate that base-induced shifts of the stretching frequencies of the X−H band of the donors in infinite dilution in inert media can also characterize the Lewis basicity of the corresponding pure bases as solvents".

C. β scales are based on the concept of the "solvatochromic comparison method" set forth by Kamlet and Taft.[19] The first fundamental assumption of the solvatochromic comparison method is that the same linear relationship holds for the nonspecific part of the solvent effect in the presence of hydrogen bonding. The second is that this contribution is proportional to the value of the π^* parameter for the solvent S under scrutiny.

From the positions of the solvatochromic bands of the hydrogen-bonding donor indicator *i*, and its homomorph *j* in solvent S, respectively $\sigma_{\mathrm{S}}(i)$ and $\sigma_{\mathrm{S}}(j)$, it was found that eq 17 holds for non-hydrogen-bonding solvents:

$$\sigma_{\mathrm{S}}(i) = a_{ij}\sigma_{\mathrm{S}}(j) + b_{ij} \quad (17)$$

The experimental value of $\sigma_{\mathrm{S}}(i)$ for a hydrogen-bonding acceptor solvent is significantly different from the predicted value obtained by using eq 17. The difference, $\Delta\sigma_{\mathrm{S}}(i) = [\sigma_{\mathrm{S}}(i)]_{\mathrm{exptl}} - [\sigma_{\mathrm{S}}(i)]_{\mathrm{pred}}$, has been used to "measure" the hydrogen-bonding acceptor character of the solvent. Initially, the compound pairs 4-nitrophenol/*p*-methoxynitrobenzene and 4-nitroaniline/*p*-(diethylamino)nitrobenzene were used as indicators. The β scale of hydrogen-bonding basicity was constructed on the basis of the scaled $\Delta\sigma_{\mathrm{S}}(i)$ values determined for these indicators ($\beta = 0$ for $\mathrm{c\text{-}C_6H_{12}}$ and $\beta = 1$ for HMPA) and showed that these "solvatochromic betas" correlate to a high degree of precision with the logarithms of the equilibrium constants for the 1:1 hydrogen-bonding associations between 4-fluorophenol or phenol and a large number of bases in $\mathrm{CCl_4}$ solution.[19]

Laurence, Nicolet, and Helbert,[56] in a study of solvatochromic indicators, showed that *p*-(dimethylamino)nitrobenzene is a better indicator than *p*-(diethylamino)nitrobenzene. Furthermore, they were able to compare the homomorphic couples 4-nitrophenol/4-methoxynitrobenzene and 4-nitroaniline/4-(dimethylamino)nitrobenzene in a series of studies performed on purified and dried solvents at 25.0 °C and 0.1 MPa. They confirmed that in the absence of hydrogen-bonding interactions, the linear relationship between the positions of the homomorphic indicators holds to an extremely high degree of precision.

Abboud and Notario,[16] by strictly applying the solvatochromic comparison method to each of these homomorphic couples, determined and compared the β values for all of the solvents for which data were available. They presented their results as β_{OH} (4-nitrophenol/4-methoxynitrobenzene) and $\beta_{\mathrm{NH_2}}$ (4-nitroaniline/4-(dimethylamino)nitrobenzene) values. This comparison showed that, although the hydrogen-bonding acceptor rankings defined by these parameters are roughly similar, the linear relationship between β_{OH} and $\beta_{\mathrm{NH_2}}$ is solvent family dependent.

D. The SB scale was developed by Catalán et al. in 1996[57] by applying the solvatochromic comparison method to the pair of homomorphs 5-nitroindoline and 1-methyl-5-nitroindoline. The authors used the difference between the positions of the longest wavelength absorption band of these homomorphs in the UV-vis region as a quantitative measure of the hydrogen-bonding acceptor character of the solvent. The value of the normalized parameter SB ("solvent basicity") for any given solvent is defined through eq 18, wherein $\Delta\sigma$ (gas phase) was obtained by extrapolation of the $\Delta\sigma$ values for *n*-alkanes and TMG (tetramethylguanidine). TMG leads to the largest hydrogen-bonding basicity effects in their study. Catalán et al.[57] observed that (with the single exception of pyridine), SB and β_{OH} correlate to a satisfactory degree of precision.

$$\mathrm{SB} = [\Delta\sigma\,(\mathrm{solvent}) - \Delta\sigma\,(\mathrm{gas\ phase})]/[\Delta\sigma\,(\mathrm{TMG}) - \Delta\sigma\,(\mathrm{gas\ phase})] \quad (18)$$

E. The σ_{CO} and $\Delta\sigma_{\mathrm{CO}}$ scales are based on a study published in 1987 by Nicolet, Laurence, and Luçon[43] on the solvent shifts undergone by the C=O stretching band of methyl trichloroacetate ($\mathrm{CCl_3COOMe}$) and trichloroacetic acid ($\mathrm{CCl_3COOH}$). The authors applied the "IR comparison method" to the above-mentioned pair. The basic concepts of this method are as follows: (i) for solvents that are not or only extremely weak hydrogen-bonding acceptors and for the gas phase, the positions of the C=O stretching bands of both compounds are linearly related to a high degree of precision, and (ii) the hydrogen-bonding basicity of a hydrogen-bonding acceptor solvent is given by the difference between the experimental value of $\sigma(CCl_3COOH)$ and the value calculated by means of eq 18.

2.2.3. Multiparameter Approaches

Katritzky et al.[8] tested various multiparameter equations using linear combinations of existing empirical solvent parameters. They combined successfully E_T values with functions of the dielectric constant and index of refraction. Using E_T and the Kirkwood function $(\epsilon_r - 1)/(2\epsilon_r + 1)$, a two-parameter equation was constructed that allows independent variation of dipole/dipole and hydrogen-bonding forces. This equation is based on the assumptions that the Kirkwood function adequately represents dipole/dipole interactions and that E_T values are sensitive to both dipolar interactions and the interaction between solute and hydrogen-bond donor solvents.

Koppel and Palm[9,58] used eqs 19−24 to define four parameters for characterizing solvents: polarity (Y), polarizability (P), electrophilicity/acidity (E), and nucleophilicity/basicity (B).

In the following, the functions $(\epsilon - 1)/(2\epsilon + 1)$ or $(\epsilon - 1)/(\epsilon + 2)$ are denoted by Y ("polarity") (eqs 19a and 19b), and the function $(n^2 - 1)/(n^2 + 2)$ is denoted by P ("polarizability") (eq 20).

$$Y = (\epsilon - 1)/(2\epsilon + 1) \tag{19a}$$

or

$$Y = (\epsilon - 1)/(\epsilon + 2) \tag{19b}$$

$$P = (n^2 - 1)/(n^2 + 2) \tag{20}$$

The authors found that a rather satisfactory linear relationship exists between functions $(\epsilon - 1)/(2\epsilon + 1)$ and $(\epsilon - 1)/(\epsilon + 2)$.[9] According to Koppel and Palm, in practice the choice between these different formally equivalent dielectric functions is arbitrary and depends more on scientific traditions of the general application of these functions in physics and chemistry and on personal preference. Equation 19a, as function of ϵ, and eq 20, as function of n, were preferred for correlations of the contributions of nonspecific solvation to solvent effects on $\Delta\nu$ (IR spectra), log(solubility) values, etc. In their treatment of solvatochromic shifts in electronic spectra, eqs 19b and 20 were used.

Using these two parameters, Y and P, the authors have performed a least-squares regression analysis of the chemical and spectroscopic data according to eq 21, where A is the solvent-sensitive characteristic for a given process, Y and P are the above-defined functions of ϵ and n, and A_0, y, and p are the regression coefficients. According to its physical meaning A_0 is equal to the A value, for the gas phase ($\epsilon = n = 1$ for a vacuum, and $Y = P = 0$), and y and p represent the susceptibilities of the process to the influences of solvent polarity and polarizability, respectively.

$$A = A_0 + yY + pP \tag{21}$$

Consequently, subtraction of the corresponding polarity (yY) and polarizability (pP) contributions from the total solvent effect has led the authors to the definition of a contribution, ΔA_{sp}, from specific solvent-solute interactions, eq 22.

$$\Delta A_{sp} = A - A_0 - yY - pP \tag{22}$$

According to eq 22 the electrophilic solvation power, E, of the solvent has been defined by eq 23, where E_T is Dimroth's solvent polarity parameter, based on the solvent-dependent electronic $\pi \rightarrow \pi^*$ transitions for N-phenolpyridinium betaines.

$$E = E_T - 25.57 - 14.39Y - 9.08P \tag{23}$$

The fourth parameter developed by Koppel and Palm, nucleophilicity/basicity (B), has been discussed before (see section 2.2.2.3.A, eq 15).

They used these four parameters to build one of the best known of the multiparameter solvent scales or linear free energy relationships (LSER). The multiparameter equation describing both the nonspecific (Y, P) and specific (E, B) components of solvent−solute interactions sometimes also contains the isosteric effect of solvent molecules (eq 24), where e and b characterize the sensitivity of a given process toward electrophilic and nucleophilic solvation effects, respectively. The conditions $e = 1$ and $b = 1$ hold for the reference processes, that is, the $\pi \rightarrow \pi^*$ transitions for N-phenolpyridinium betaine and IR stretching frequency shifts of CH_3OD, respectively. The equation has been applied to the description of some 60 solvent-dependent properties with good results.[9]

$$A = A_0 + yY + pP + eE + bB \tag{24}$$

An empirical two-parameter approach for the description of solvent effects has been proposed by Krygowski and Fawcett.[21] Considering that only specific solute/solvent interactions need to be considered, the authors postulated that the solvent effect on a solute property A can be represented as a linear function of only two independent but complementary parameters describing the Lewis acidity and Lewis basicity of a given solvent. These parameters were chosen to be the E_T values (as a measure of Lewis acidity) and Gutmann's donor numbers (DN) (as a measure of solvent basicity) (eq 25), wherein α and β are regression coefficients describing the sensitivity of the solute property A to electrophilic and nucleophilic solvent properties, respectively. The regression coefficients were normalized.

$$A = A_0 + \alpha E_T + \beta(\mathrm{DN}) \tag{25}$$

Swain et al.[24] have also given a two-parameter treatment of solvent effects. According to their study all solvent effects can be rationalized in terms of two complementary solvent property scales, one measuring the solvent's anion-solvating tendency or "acity" (A_j) and another measuring the solvent's cation-solvating tendency or "basity" (B_j) (eq 26). A_j and B_j characterize the solvent j; A and A_0 as well as the multiple regression coefficients a_i and b_i depend only on the solvent-sensitive solute property i under study. Constants a_i and b_i represent the sensitivity of solute property i to a solvent change. The authors used a nonlinear least-squares procedure to evaluate and optimize all constants for 1080 data sets in order to get the best possible fit consistent with eq 26.

$$A = A_0 + a_iA_j + b_iB_j \qquad (26)$$

Mayer[25] introduced a semiempirical multiparameter relationship, eqs 27a and 27b, for the description of solvent effects on the thermodynamics and kinetics of chemical reactions, wherein ΔG represents the Gibbs energy of reaction or activation ($\Delta G^{\#}$), DN the donor number, AN the acceptor number,[59] and $\Delta G_{\mathrm{vp}}{}^{0}$ the standard molar Gibbs energy of vaporization of a solvent S and a reference solvent R, respectively. Acetonitrile was used as a reference solvent ($\Delta G_{\mathrm{vp}}{}^{0}$ = 5.31 kJ/mol).[25]

$$\Delta G^{\mathrm{S}} - \Delta G^{\mathrm{R}} = a(\mathrm{DN}^{\mathrm{S}} - \mathrm{DN}^{\mathrm{R}}) + b(\mathrm{AN}^{\mathrm{S}} - \mathrm{AN}^{\mathrm{R}}) + c(\Delta G_{\mathrm{vp}}{}^{0\mathrm{S}} - \Delta_{\mathrm{vp}}{}^{0\mathrm{R}}) \qquad (27a)$$

$$\Delta\Delta G = a[\Delta(\mathrm{DN})] + b[\Delta(\mathrm{AN})] + c[\Delta\Delta \mathrm{G}_{\mathrm{vp}}{}^{0}] \qquad (27b)$$

Dougherty[26] developed a multiparameter correlation by considering the interaction between the highest occupied orbitals (HOMO) of the solvent and the ions and the corresponding lowest unoccupied orbitals (LUMO) of the ions and the solvent. The energies of these orbitals were approximated from ionization potentials and electron affinity data.

Another multiparameter equation for the correlation of solvent effects on physicochemical properties has been proposed by Drago:[60,61]

$$\Delta\chi = W + E^*{}_{\mathrm{A}}E_{\mathrm{B}} + C^*{}_{\mathrm{A}}C_{\mathrm{B}} + PS' \qquad (28)$$

where S' is the "universal" descriptor of solvent polarity according to Drago, P is a solute parameter intended to measure the susceptibility of the solute probe to polarity, and W is a nonzero intercept at S' = 0. With the $E^*{}_{\mathrm{A}}E_{\mathrm{B}}$ and $C^*{}_{\mathrm{A}}C_{\mathrm{B}}$ terms, eq 28 includes the well-known E/C equation of Drago 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, $E^*{}_{\mathrm{A}}E_{\mathrm{B}}$ and $C^*{}_{\mathrm{A}}C_{\mathrm{B}}$, which are said to correspond to the strength of electrostatic and covalent contributions in the acid/base interactions, respectively.[62]

2.2.3.1. Linear Solvation Energy Relationships (LSER). Linear Gibbs energy relationships are known as "extrathermodynamic" combinations of detailed models with thermodynamic concepts. This approach to model building lacks the rigor of thermodynamics, but it can provide information not otherwise accessible. Although linear Gibbs energy relationships are not a necessary consequence of thermodynamics, their wide occurrence suggests that the nature of this connection between the correlated quantities can usefully be explored.[3] The functional relationships between substituent or solvent parameters and various substituent- or solvent-dependent processes take the form of linear Gibbs energy relationships, frequently still known as linear free energy relationships (LFER).

One of the best-known LFERs is the Koppel–Palm multiparameter equation described in the previous section.

Taft et al.[63] introduced the term linear solvation energy relationships for generalized treatment of solvation effects, which assumes that attractive solute-solvent interactions are frequently of two kinds: (i) nonspecific dipolarity/polarizability[64] and (ii) specific hydrogen-bond complex formation.[19] Class ii is subdivided into solute hydrogen-bond donor (HBD)/solvent hydrogen-bond acceptor (HBA) complexing and (the converse) solute HBA/solvent HBD complexing. LSER further assume linear free energy or electronic energy relationships for each of the contributing terms to the observed solvent effects. The potential relevance of each contribution is judged by knowledge and theoretical concepts of effects of the molecular structure on solutes and solvents and the nature of the measured property. The defining measured properties are molecular properties (e.g., dipole moments), spectroscopic solvent shifts, or molecular affinities, which are measured by formation constants.

The "solvatochromic parameters" describing solute and solvent properties, which have been widely used by Kamlet, Abboud, Abraham, and Taft in their studies,[19,20,63] comprise the following terms.

π^*, a measure of solute or solvent dipolarity/polarizability, estimates the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. For "select solvents" (i.e., nonprotonic aliphatic solvents with a single dominant bond dipole), π^* values are proportional to the dipole moment of the solvent molecule.[65] The π^* scale was selected to run from 0.0 for cyclohexane to 1.0 for dimethyl sulfoxide.

δ, a discontinuous "polarizability correction term", is equal to 0.0 for non-chlorine-substituted aliphatic solvents, 0.5 for poly-chlorine-substituted aliphatics, and 1.0 for aromatic solvents. δ values reflect the observation that differences in solvent polarizability are significantly greater among the three solvent classes than within the individual classes.[66]

α, a scale of HBD acidities, applies to self-associating compounds when they act as solvents. α describes the ability of a solvent to donate a proton in a solvent-to-solute hydrogen bond. The α scale was selected to extend from 0.0 for non-hydrogen-bond donor solvents to ~1.0 for methanol.

α_{m} applies to self-associating compounds when they are acting as "monomeric" solutes.

β, a scale of HBA basicities, applies to self-associating compounds when they act as solvents. β describes the solvent's ability to accept a proton or donate an electron pair in a solute-to-solvent hydrogen bond. The β scale was selected to extend from 0.0 for non-hydrogen-bond donor solvents to ~1.0 for hexamethylphosphoric acid triamide (HMPT).

β_m applies to self-associating compounds when they are acting as "monomeric" solutes.

ω, an amphiprotic hydrogen-bonding parameter, is used for amphiprotic compounds in aqueous solution in place of β. For unsubstituted alkanols, $\omega \cong \beta_m$.

δ_H is the Hildebrand solubility parameter; δ_H^2 measures the solvent's contribution to the cavity term and corresponds to the cohesive pressure c, which characterizes the energy associated with the intermolecular solvent/solvent interactions. Thus, δ_H^2 is considered as a measure of the enthalpy or Gibbs energy input required to separate solvent molecules to provide a suitably sized cavity for the solute.

V, the solute molar volume, is usually defined as the molecular weight divided by the liquid density at 25 °C. V measures the solute's contribution to the cavity term. The authors[67] used $V/100$ so that the cavity parameter covered roughly the same range as the dipolarity/polarizability and hydrogen-bonding parameters, which makes easier the evaluation of the contributions of the three types of effects to the solubility property studied.

ξ is a coordinate covalency parameter used to correlate certain types of so-called family-dependent solute basicity properties.[20,68] The ξ values are interpreted as being approximate measures of the relative coordinate covalencies of the bonds that are formed between solute and solvent at the base center of the solvent. Coordinate covalencies of solute/solvent adducts of a given solute acid decrease in strength (ξ decreases) as the electronegativity of the solvent base center increases, because the positive charge created by coordinate covalency on an increasingly electronegative atom is unfavorable; ξ reconciles the β scale with the pK_a scale.

$$XYZ = XYZ_0 + \text{cavity term} + \text{dipolar term} + \text{hydrogen-bonding term} \quad (29)$$

A large number of solubility and solvent-dependent properties,[69] XYZ, depend on three terms as shown in eq 29. Here the cavity term measures the free energy or enthalpy input required to separate the solvent molecules to create a suitably sized cavity for the solute. The dipolar term measures the exoergic effects of solute/solvent dipole-dipole, dipole-induced dipole, and mutually induced dipole interactions. The hydrogen-bonding term measures the exoergic effects of hydrogen-bonding (or Lewis acid/base) complexation between the solute and the solvent.

Equation 29 with solvatochromic parameters appropriately included becomes eq 29a, where the subscript 1 is applied to the solvent and subscript 2 to the solute.

$$XYZ = XYZ_0 + A(\delta_H^{\,2})_1 V_2/100 + B\pi^*{}_1\pi^*{}_2 + C\alpha_1(\beta_m)_2 + D\beta_1(\alpha_m)_2 \quad (29a)$$

When the effects of multiple solvents on a single solute or set of reactants are involved, correlations are expressed in terms of the solvatochromic parameters of the solvents (eq 29b).

$$XYZ = XYZ_0 + h(\delta_H^{\,2})_1 + s\pi^*{}_1 + a\alpha_1 + b\beta_1 \quad (29b)$$

When the solubility properties of multiple solutes in single solvents or distributions between pairs of solvents are involved, the correlations are expressed in terms of the solvatochromic parameters of the solutes (eq 29c).

$$XYZ = XYZ_0 + mV_2/100 + s\pi^*{}_2 + b\beta(\text{or } \beta_m \text{ or } \omega)_2 + a\alpha(\text{or } \alpha_m)_2 \quad (29c)$$

When aromatic and aliphatic solutes or solvents are included in the same correlation, the δ parameter often needs to be used in conjunction with π^*.[66] For certain types of "family-dependent" basicity properties,[20,63] the ξ parameter needs to be used in conjunction with β.

XYZ properties analyzed by Kamlet and Taft have included solubilities of various type solutes in chemical solvents and biological tissues and fluids and free energies of solution and of transfer between solvents among the diverse properties, which have been correlated.

This work has been documented in an impressive series of more than 40 articles titled "Linear Solvation Energy Relationships" and has appeared: Part 1[70] ... Part 44.[71]

Abraham and co-workers[72] performed an analysis of solute hydrogen-bond basicity in terms of complexation constants (log K) using F_1 and F_2 factors, the principal components of different kinds of basicity. The authors used two constants, S_1 and S_2, to define an angle θ as a measure of the electrostatic covalent bonding ratio in the hydrogen-bond complex. Abraham observed that among a wide range of reference acid/solvent systems, θ varies only from 64 to 73°, and he suggested that a reasonably general scale could be set up for bases using these reference systems.

Additionally, Abraham et al.[73] set up two scales of solvent hydrogen-bond basicity: (i) β_1 (general), constructed using the solvatochromic indicator method and a series of double-regression equations (for 11 aniline-type indicators), and (ii) β_1 (special), constructed by the homomorphic comparison method using only 4-nitroaniline and 4-nitro-*N*,*N*-dimethylaniline as indicators. The authors showed that although there is a general connection between these two solvent hydrogen-bond basicity scales and the so-called solute scale, β_2 (pKHB), obtained from log K values for hydrogen-bond complexation of bases with 4-fluorophenol in CCl_4, the use of β_1 to predict β_2 and vice versa is a very hazardous procedure.

By using the β_2H scale of solute hydrogen-bond basicity, formulated from 1:1 hydrogen-bond complexation constants in CCl_4, Abraham[74] formulated a scale of effective or summation hydrogen-bond basicity. The method used by the author is based on eq 30, where SP is a set of solute water-solvent

$$\log \mathrm{SP} = C + rR_2 + s\pi_2\mathrm{H} + a\Sigma\alpha_2\mathrm{H} + b\Sigma\beta_2 + vV_x \qquad (30)$$

partition coefficients in a given system, R_2 is an excess molar refraction, π_2H is the solute dipolarity/polarizability, $\Sigma\alpha_2$H and $\Sigma\beta_2$ are the effective solute hydrogen-bond acidity and basicity, and V_x is McGowan's characteristic volume.

2.2.3.2. Statistical Scales. Statistical scales are in principle "model-independent". They are constructed by statistically averaging medium effects on the physical properties or reactivity data of a wide number of solutes. The choices of the solutes and/or properties represent potential limitations of these scales.

A and *B* scales were defined in 1983 by Swain et al.,[24] who analyzed 1080 data for 61 solvents and 77 reactions according to the bilinear model described by eq 31, wherein P(S) is the value taken by property

$$P(\mathrm{S}) = aA(\mathrm{S}) + bB(\mathrm{S}) + \mathrm{c} \qquad (31)$$

P in solvent S; a, b, and c are constants depending only on the solute and the property under consideration. A and B are, respectively, the anion-solvating ("acity") and the cation-solvating ("basity") tendencies of S. The A and B values were determined from statistical study of the database indicated above together with boundary conditions: $A = B = 0$ for n-heptane, $A = B = 1$ for water, $A = 0$ for HMPA, and $B = 0$ for trifluoroacetic acid. Both non-hydrogen-bond donors and hydrogen-bond donors were involved in this study. Analysis of these two scales shows that they both fail to comply with the mathematical condition of orthogonality that should have been imposed, and neither conveys accurately the putative physical meaning intended.[16]

B. S′ was introduced by Drago in 1992[60] and is based on the statistical treatment of 30 molecular probes and 31 solvents. The data were analyzed on the basis of the correlation of eq 32, wherein $\Delta\chi$

$$\Delta\chi = S'P + W \qquad (32)$$

stands for the effect of the solvent on the physicochemical property under consideration, S' is the "universal" descriptor of solvent polarity conforming with Drago, P is a solute parameter intended to measure the susceptibility of the solute probe to polarity, and W is a nonzero intercept at $S' = 0$.

2.3. Detailed List of Solvent Scales with References and Number of Solvents

Table 1 presents a detailed list of solvent scales collected from the literature,[8,9,14,24,27,30,38,39,47−49,51,53,55,57,61,62,75−194] together with the number of solvents involved in the development of every scale, the physical background, and main authors.

Analysis of the data in Table 1 demonstrates that 44% of the scales are developed using spectroscopic measurements, 15% use equilibrium, and 13% use kinetic measurements, and those based on other methods represent 28% from a total of 184 classified solvent scales.

The number of solvents used for developing a solvent scale has varied from 5 to >100. Understandably, the larger data sets were used for spectroscopic measurements and the smaller ones for equilibrium (except Gutmann's scale, DN) and kinetic measurements.

Consequently, existing solvent scales based upon spectroscopic measurements are more commonly used than others.

A disadvantage of most of the scales of Table 1 is that in addition to nonspecific effects, they contain specific effects, which are unique to the probe (solute) used to develop each scale. As a result, each scale differs for reasons that are not obvious, and this inhibits the understanding of solvent influence on new solutes.

Moreover, many of the scales presented above are limited to a specific range of solvent polarity or other property due to restrictions in the methodology of their measurements: for instance, the probe compound can become insoluble or unstable under some conditions. This means that any individual solvent is rarely represented in all common scales and no scale covers all common solvents.

There are other criteria describing the quality of an individual solvent scale besides the number and range of solvents it holds or the limitations on the expansion introduced by the probe itself. For instance, spectroscopic scales can be compared according to the solvatochromic range (sensitivity to polarity change of the absorption band under investigation) of their respective probes. Obviously, the larger the shift of the band, the higher can be the possible accuracy/sensitivity of the scale derived from this shift. A number of probe molecules together with their solvatochromic range have been compiled by Reichardt.[62] The $E_T(30)$ scale is representative of a scale based on probes with an outstandingly high solvatochromic range (-9730 cm^{-1}), some 5 times larger than the range of the probe of Φ (-1865 cm^{-1}).

The necessary concentration of the probe molecules for the measurement may serve as another parameter for the comparison of scales. If the absorption bands can be produced only in relatively high concentrations, interaction and even aggregation of the probes may occur, making assumptions of pure solvent polarity dependence questionable. The concentration problems are also often common to scales based on NMR measurements.

The solubility of the probes often sets limits on the range of solvents in a scale; a common practice is to use (an) additional probe(s) with better solubility for the extension of the scale. The loss of accuracy comes from the fact that the correlation between the transitions energies of the probes used is seldom perfect; unfortunately, all of the values of a scale are commonly assigned the same precision. The same is often true for scale values that are measured at some other temperature. Although some model processes are independent of temperature, some others have strong dependencies, and the corresponding scale values should not be attributed the same precision as others.

Several scales were introduced a long time ago. Experimental techniques for the measurements involved in some of them have improved considerably (i.e., IR spectroscopy measurements for the *G* scale, calorimetry for DN). It would now be possible to remeasure the values for these scales and, thus, improve their accuracy.

The last but not least criterion is the general clarity of the model process. It is rather important to understand which types of interactions are present between the solvent and the probe. A good model process should involve predominantly the same type of interactions over the whole range of solvents. Over the years, overall progress in chemical understanding, including the development of quantum chemistry, has considerably reduced uncertainties of the possible types of interaction as has been illustrated for the case of basicity scales.[195]

2.4. Attempts To Relate Scales to Descriptors

A main objective of solvent polarity scales is to facilitate the systematic correlation and analysis of chemical and physicochemical properties in solution. The macroscopic (bulk) properties of chemical compounds clearly depend on their microscopic (structural) characteristics. It has not been possible to define solvent polarity in terms of macroscopic solvent properties, and as a result many empirical solvent polarity scales have evolved as an alternative approach for predicting or analyzing solvent effects (see Table 1).

The ability to calculate free energy changes associated with solvation allows calculation of differential free energies in solution without having to model complex changes in hydrogen-bonding networks, conformational changes, or other differential solvation issues for which there is little direct information.[196]

Recently, significant effort has been directed in trying to model and relate complex solvent effects to solvent scales using fundamental molecular properties or descriptors: both empirical and theoretical.

The LSER descriptors based on LFER are demonstrated to be successful in correlating a wide range of chemical and physical properties involving solute-solvent interactions of compounds.[65,197] The coefficients of the descriptors in the correlation equations are expected to provide insight into the physical nature of the solute−solvent interactions related to the experimentally observed phenomena or data. The original LSER descriptors (also called the solvatochromic descriptors) were derived from UV-vis spectral shifts of indicator dyes. Thus, their ability to make a priori predictions has been somewhat limited because of their empirical origin. Although there exist tables of LSER parameters and predictive relationships to help in their estimation, LSER descriptors for new compounds are not easily defined. Attempts to correlate computationally derived structural and electronic descriptors with the solvatochromic parameters have met with only moderate success.[198]

In 1987, on the basis of two distinct studies, Abraham et al. showed that (i) solvolysis/dehydrohalogenation rates of $(CH_3)_3CCl$ in 21 HBD and non-HBD solvents are correlated by an LFER in terms of δ_H^2 (solvent cohesive energy) and π, α, and β (the solvatochromic parameters that scale solvent dipolarity−polarizability, hydrogen-bond-donor acidity, and hydrogen-bond-acceptor basicity);[199] (ii) at least four solvent parameters are needed in any general equation to model solvent effects on rate constants or on Gibbs energies of individual solutes: as parameters in the general equation they used π^* (the solvent dipolarity), α (the solvent hydrogen-bond acidity), β (the solvent hydrogen-bond basicity), and δ_H^2 (the solvent cohesive energy).[200]

In an approach to circumvent problems associated with the LSER parameters, Famini and co-workers developed a new set of computationally derived descriptors, called “theoretical LSER” (TLSER).[201,202] The TLSER attempts to maintain the same relationship between property and parameters; that is, it incorporates steric, polarizability, and hydrogen-bonding terms. However, each TLSER term is derived by a semiempirical molecular orbital method, permitting a much greater degree of a priori prediction once a correlation is derived than does LSER. Like LSER, TLSER uses a single set of descriptors (six for the TLSER) and each parameter describes a single, orthogonal molecular event of characteristics.

$$\log(\gamma) = c_0 + c_1 V_{mc} + c_2 \pi^* + c_3 \epsilon_a + c_4 \epsilon_b + c_5 q^+ + c_6 q^- \quad (33)$$

The most general form of TLSER is expressed in eq 33,[202] where V_{mc} is the molecular van der Waals volume calculated according to the method of Hopfinger.[203] The polarizability term π^* is derived from the polarization volume computed by using the method of Kurtz.[204] The hydrogen-bonding effects are separated into donor and acceptor components. The covalent contribution to Lewis basicity, ϵ_b, is represented as the difference in energy between the lowest unoccupied molecular orbital (ϵ_{LUMO}) of water and the highest occupied molecular orbital (ϵ_{HOMO}) of the solute. The electrostatic basicity contribution, denoted q^-, is simply the most negative atomic charge in the solute molecules. Analogously, the hydrogen-bonding donating ability is divided into two components: ϵ_a is the energy difference between the ϵ_{HOMO} of water and ϵ_{LUMO} of the solute, whereas q^+ is the most positive charge of a hydrogen atom in the solute molecule. The advantage of using this single set of descriptors has been demonstrated in the ability to compare disparate properties and data set.

An implicit assumption of the TLSER approach is that the descriptors are “pure” and reflect a particular microscopic property without “mixing” or contamination from other descriptors. Although it is impossible to prove it in a “global” sense, most of the TLSER regressions to date have very small cross-correlations among descriptors.

Engberts et al.[205] correlated the effect of 30 solvents on the C=O stretching frequencies of several substituted 2-pyrrolidinones using the TLSER and five additional experimentally derived solvent scale methodologies.

Famini et al.[183] used TLSER methodology to correlate, illuminate, and probe eight solvent scales commonly used in LFER and physical organic chemistry. The data set consists of 30 common solvents. On the basis of the correlations obtained for these solvent scales, the Reichardt $E_N{}^T$ ($R = 0.961$), the Swain acidity, E ($R = 0.956$), and basicity, B ($R = 0.928$), the Koppel–Palm polarity, Y ($R = 0.914$), and polarizability, P ($R = 0.925$), the molar refraction, MR ($R = 0.975$), and the Gutmann acceptor number, AN ($R = 0.972$), and donor number, DN ($R = 0.917$), the authors concluded that the TLSER method can predict values for these solvent scales and provide better understanding of the underlying physical meaning of these solvent scales.

Carr and co-workers[206] examined a number of empirical single-parameter scales of solvent strength (π^*, E_T) used to correlate solvatochromic phenomena in aprotic liquids considering the effects of modeling dipole-dipole and dipole-induced dipole interactions with a single global parameter while excluding the possibility of H-bonding interactions. They concluded that the regression coefficients are often misleading and not representative of the physical system. Some years later, on the basis of the study of the relationships between the solute capacity factor and Reichardt's E_T or the Kamlet-Taft π^* scale in hydro-organic mixtures for a series of alkylbenzenes, Cheong and Carr[207] showed that at least two solvent parameters are needed to account for the cavity formation and solute-solvent interaction processes which control retention in reversed-phase liquid chromatography.

Shmidt, Mezhov, and Khananashvili compared the VR* (solvent influence) scale with (i) the empirical parameter scales developed for quantitative description of solvent characteristics (from LFER, solvent effects on chemical equilibrium, or solvent effects on reaction kinetics)[208] and (ii) Kamlet-Taft spectrophotometric π^* parameters, H_2O solubilities in immiscible organic solvents, and H_2O-solvent interfacial tensions. On the basis of these studies, the authors concluded that (i) the VR* parameter correlates linearly with the parameters of 20 other scales in the absence of specific solvation effects and (ii) the interfacial tensions could be predicted from VR* and π^* parameters.

Using several dyes, Spange and co-workers[209] estimated the empirical donor-acceptor and polarity parameters of several inorganic solids, polymers, and combinations of both on the basis of a correlation analysis of the UV-vis spectral data of the probe dyes in more than 70 protonic and nonprotonic solvents versus the acceptor number of Gutmann and the Kamlet-Taft α, β, and π^* solvatochromic parameters. Spange[210] concluded that empirical polarity parameters are recommended as useful characteristics for describing the internal and external surface properties of various solid materials, for example, synthetic polymers, native polymers, inorganic oxides, sol–gel hybrids, and composites; a general polarity scale for solid materials, based on LSER study, is suggested.

The Florida-Tartu group[211] developed a three-parameter QSPR model ($N = 25$ solvents, $R^2 = 0.936$), and Mu and Drago[212] developed a two-parameter MQSPR (model-based QSPR) model for a unified solvent polarity scale (S') on the basis of theoretical molecular descriptors, calculated using CODESSA software. The descriptors utilized in these models provide insight into the solvation process at the molecular level. Katritzky and co-workers used the three-parameter model to extend available S' values to a total of 67 solvents.

Zou and co-workers[213–215] performed ab initio calculations at the HF/6-31G* level for different data sets of solvents. The authors established linear correlations between $E_T{}^N$, π^*, Py, SPP, S', solvent softness scales, and theoretical descriptors by using multiple regression. These correlations have been analyzed from the point of view of intermolecular interactions between the “probe solute” and the solvent.

On the basis of a stepwise correlation analysis, Berthelot et al.[216] showed that the hydrogen-bond acceptor strengths of numerous bases can be formed from octanol–water partition coefficients after subtraction of a hydrophobic cavity term proportional to the molecular volume of the solutes. When one of the basic centers of the solute is hindered by bulky substituents, they observed significant deviations from the resulting two-parameter model.

In an extensive attempt to relate solvent scales to the theoretical descriptors, the Florida-Tartu group[217] used the CODESSA software to perform a quantitative structure–property relationship (QSPR) analysis of 45 different solvent scales and 350 solvents. In the attempt to obtain the optimum QSPR correlation results, scales were treated in the form of various mathematical functions: X^{-1}, X^2, X^{-2}, $X^{1/2}$, $X^{-1/2}$, X^3, X^{-3}, and log(X). For example, scales Y, SB, d, J, BB, CB, E^*_{MLCT}, D_π, and SPPN were found to be best correlated as Y^2, SB^{2-}, log(d), J^2, BB^3, CB^{2-}, $(E^*_{\mathrm{MLCT}})^3$, $D_\pi{}^3$, and $(\mathrm{SPP^N})^3$, respectively. The QSPR equations for the 45 scales treated contained altogether 118 different descriptors. Of course, some of these descriptors are very similar; for example, they can depend on the same intrinsic property of a solvent and differ only in their calculation methods, or they may derive from alternative semiempirical quantum chemical or empirical (Zefirov's) methods of calculation of the charge distribution in the molecule. Therefore, the number of independent descriptors is actually far less than 118, but in this work no attempt was made to reduce the number of descriptors by substitution of one descriptor for another similar one. The high quality of the models (32 of the 45 give $R^2 > 0.90$, whereas only two have $R^2 < 0.82$) made possible direct calculation of predicted values for any of these scales for previously unmeasured solvents. The authors showed that in most cases the theoretical descriptors involved are in good agreement with the physical concepts invoked by the original authors of the scales.

Chemometrics, or multivariate statistical analysis, is one of the most recent tools in attempts to relate solvent scales to descriptors.

Eliasson et al.[218] performed a multivariate analysis on the correlation between different solvent scales and solvent-induced ^{13}C NMR chemical shifts of a planar lithium carbanion.

Auhmani et al.[219] compared the empirical and chemometric approaches to the modeling of the solvent effects (Kamlet-Taft's π*, α, and β parameters, E_T^N of Reichardt, and A and B of Swain) on a number of NMR, IR, and UV-vis spectral properties. They concluded that the correlations have a satisfactory quality.

All of these studies indicated that the approach of relating solvent scales to different descriptors (i.e., LSER, TLSER, theoretical molecular descriptors, etc.) could finally lead to a more or less general solvent scale.

3. Interrelations between Solvent Scales

Considering the vast number of existing single- and multiple-parameter solvent polarity scales, the question of their interrelations inevitably arises. The number of independent physical parameters describing solvent-dependent processes must be limited. Consequently, most scales should be highly intercorrelated; it follows that it should be possible to describe any individual solvent polarity scale using one or several other scales.

3.1. Correlation of Solvent Scales

Comparing the solvent scales with each other may not be as trivial as it first could seem. For instance, many scales have been constructed for a rather limited range of solvents. Many probes can be used only in certain types of solvents: in one solvent they could be insoluble, unstable, or enter into undesirable side reactions. Several authors have used a combination of probes or extrapolation to overcome this difficulty and to get a reasonably extensive and, therefore, a generally applicable solvent scale. Another hindrance for the comparison of solvent scales is the range of their values. Many scales were proposed in a normalized form (typically between the values 0 and 1); others were presented the same way as they came from their respective equations or were normalized between some other boundaries. Thus, before any comparison or statistical analysis of solvent scales, they should desirably be normalized around some predefined value.

In many cases, authors presenting a new study of some solvent-dependent process, which might find use as a solvent scale, compare and correlate their data with some well-known solvent polarity scale. Usually a limited number of other scales are considered, and frequently there are too few solvents common to the different scales to make the comparisons completely clear and reliable. Several authors have correlated one or two scales against some other scale; we mention only a selection of these studies, concentrating of the more extensive correlations available.

Frequently, the analysis of scales taken from different sources does not result in high correlations. One reason can be the choice of solvents. Two solvent parameters may have a high correlation coefficient when a single family of solvents is considered (hydrogen-bond donors, or electron pair donors, or nonpolar aprotic, etc.). However, two or three lines may be obtained, which can be parallel, crossing, or even orthogonal when the whole range of solvents is considered.[220] A good correlation between two solvent scales means that the blend of different interaction forces between the solvent and the solute must be similar. In the case of a diverse set of solvents and mismatching solvent scales, the relationship could be something other than linear, for example, logarithmic.

Earlier attempts to intercorrelate solvent scales are reviewed in a comprehensive study by Griffiths and Pugh.[220] These authors analyzed correlations of the E_T and Z scales. They compared the predicted Z values with those they measured themselves: 10 of the 16 solvents had the calculated value within 2% of the observed value with the rest also being reasonably close. They concluded that by using good linear correlations, nonmeasured or immeasurable solvent scale values could be calculated reliably.

Analysis of relationships between the E_T scale and other scales and solvent-dependent processes presented by Reichardt[3] shows good correlations for several processes, especially for non-hydrogen-bond donor solvents.

Redondo et al.[221] examined the G scale in detail and correlated the values of 36 solvents (also separately nonhydroxylic and nonacidic solvents) with the E_T scale, Koppel and Palm parameters (Y, P, and E), and Kamelt and Taft parameters (π* and α). They found the Kamlet and Taft treatment to be superior to others and appropriate to predict nonmeasurable values for the G scale. They concluded that the G scale is a measure of the combination of solvent polarity-polarizability (π* and $P + Y$) and acidity (E and α).

Buncel and Rajagopal[49] compared their π^*_{azo} scale with the π* scale for the ability to describe the variation in other polarity scales. They found that the π^*_{azo} scale is slightly better for the overall description of solute-solvent interactions than the popular π* scale, except for aromatic nitro compounds (the primary solute type for the π* scale). Their correlation shows that the π^*_{azo} scale based on azo merocyanines correlates better with (i) scales based on structurally similar dyes and (ii) dyes that are structurally similar to azo merocyanines.[50]

A comprehensive study and a detailed analysis of series of Lewis basicity (electron pair donating) scales were carried out by Sandström et al.[195] Correlations with their D_S scale as well as between other scales are presented and discussed. They stressed the importance of the softness/hardness concept in donor-acceptor interactions. They often found a nonlinear (e.g., logarithmic) dependence between soft acceptor and hard acceptor based basicity scales. Several inconsistencies and shortcomings in basicity scales were analyzed. Hard acceptor based scales are more common and correlate well among themselves. The use of ΔH_{BF_3} as a hard donor scale is recommended over D_N, Cu λ_{max}, and CP. The best overall soft donor scale was found to be D_S over μ, B_{soft}, and SP. Hydrogen-bond acceptor properties were found to be well described by the β_1 scale and, in specific cases, the log K_β and β_{sm} scales. Other basicity scales (multiparameter scale E and C, $\Delta\delta$) were found to have rather limited use.

Sometimes, careful correlation analysis of several solvent scales reveals experimental or derivational shortcomings for some data points. Water is a solvent of unique chemical nature; solvent polarity values for water are frequently obtained indirectly, by extrapolation from data of binary mixtures, or by using other probes, or by correlation with other similar scales. For instance, the Z value of water (94.6) was analyzed by Griffiths and Pugh[220] and found to be too large; correlations with other scales (Y and ΔR) suggested a lower value by some 3 kcal/mol. It could prove useful to remeasure the values of widely used scales proposed many years ago before any correlation analysis and statistical expansion of these scales is done as experimental techniques and equipment have often much improved since.

3.2. Overall Dimensionality of Solvent Parameters

There are several possible statistical approaches for the analysis and reduction of the dimensionality of solvent scales.

3.2.1. General Statistical Approaches

One of the simplest approaches is to test all proposed "general" multiparameter scales to verify their ability to fit the data of all the other scales. In general, this is already carried out in the course of establishing each new scale (by correlating with several other known scales), and the information from this approach is already available.

Another treatment is pairwise linear correlation analysis between each of the individual scales to find out the most and least intercorrelated ones: this groups scales according to their interrelation and, thus, indicates the most relevant elements of solvent effects for each scales. Also, any scale with all intercorrelations below some predefined threshold value can then be considered to represent a new independent solvent parameter, not sufficiently described by any other scales.

Marcus[14] studied nine solvent parameters, α, β, π^*, $E_T(30)$, DN, AN, Z, acidity, and basicity, and found several to be highly interrelated. He concluded that there were four essentially independent solvent parameters: hydrogen-bond donation ability (described best by α), hydrogen-bond acceptor ability (β), polarity/polarizability (π^*), and solvent stiffness (δ_H^2).

Sergent et al.[222,223] developed an "informative" approach, an optimum design methodology, to compare two empirical sets of solvent scales, those of Koppel and Palm (KP) and of Kamlet, Abboud, and Taft (KAT), with the purpose to determine if they are identical, similar, or quite distinct. The experimental results used in the comparison were the keto/enol equilibrium constants of 2,4-pentanedione determined by ^{1}H NMR spectroscopy. The conclusion was that both sets of scales are similar, one being more precise (KP) and the other more robust (KAT).

Catalán[122] found a significant correlation between the SPP scale and the π^* scale by Kamlet, Abboud, and Taft for a set of 67 solvents. He also correlated the E_{pNA} scale[224] with five other well-known solvent scales [$E_T(30)$, π^*, P_y, S', and SPP].[225] The work of Famini and Wilson[183] of the application of the TLSER methodology was discussed in the previous section.

Malavolta et al.[226] analyzed various polarity scales and their linear combinations for about 50 solvents in terms of the sum of Gutmann's donor and acceptor numbers (AN + DN). No correlation was obtained with Hildebrand's solubility parameter, δ, and Kamlet-Taft's π^* scale. A moderate correlation was found between AN + DN and the solvatochromic $E_T(30)$ scale ($r = 0.7374$). Notably, the best correlation was found with the combination of Kamlet-Taft's parameters $\alpha + \beta$ ($r = 0.9251$), indicating considerable similarity. Mancini et al.[227] have analyzed the relationship between different solvatochromic polarity scales (π^*_{OMe}, π^*_{NMe2}, π^*_2, and E_T^N) in a number of binary solvent mixtures: they found significant two-parameter correlations for π^*_{OMe} and π^*_{NMe2} with π^*_2 and E_T^N. This result is not unexpected because of the similarity of indicator processes used in the definition of the respective scales.

Palm and Palm chose a different approach in their study of the total number of independent variables for solvent-dependent processes. They picked a small initial set of "fundamental" scales and extended it by means of the SMIRC procedure[228] to include nine "purified" solvent parameter scales; later they reduced their model to eight parameters, claiming that it accounted for all of the dimensionality of solvent-dependent processes. The authors concluded that the stability of their results indicates a rather universal applicability and sufficiency of this set of solvent parameters. Their treatment found Y, P, δ_H^2, B, $E_T(30)$, π^*, β, and α to be statistically significant; their residual scales are somewhat different from the original ones due to the purification process. An extensive set of 359 solvent-dependent processes was then correlated using their model[229,230] with rather good results.

3.2.2. Principal Component Analysis (PCA) Approach

Another option for treating this type of dimensionality and interrelation questions is the conventional PCA. Chastrette and Carretto applied PCA to analyze[231] and to calculate empirical parameters of solvent polarity starting with the physicochemical properties of the solvents;[232] Chastrette and coworkers[233] used multivariate statistical treatment to classify 83 solvents using eight solvent parameters (K, MR, δ, μ, n_D, bp, ϵ_H, and ϵ_L), but their focus was mainly on the grouping of solvents rather than solvent scales. Nevertheless, from the intercorrelation of the solvent parameters they concluded that fewer than eight parameters should be sufficient to describe the whole dimensionality.

Maria et al.[234] studied the basicity-dependent behavior in the condensed phase of nonprotogenic organic molecules commonly used as solvents. PCA of a set of basicity-dependent properties was applied to hydrogen-bonding, proton-transfer, and interactions with hard and soft Lewis acids, including the $-\Delta H°_{BF_3}$ basicity scale. One of the conclusions was

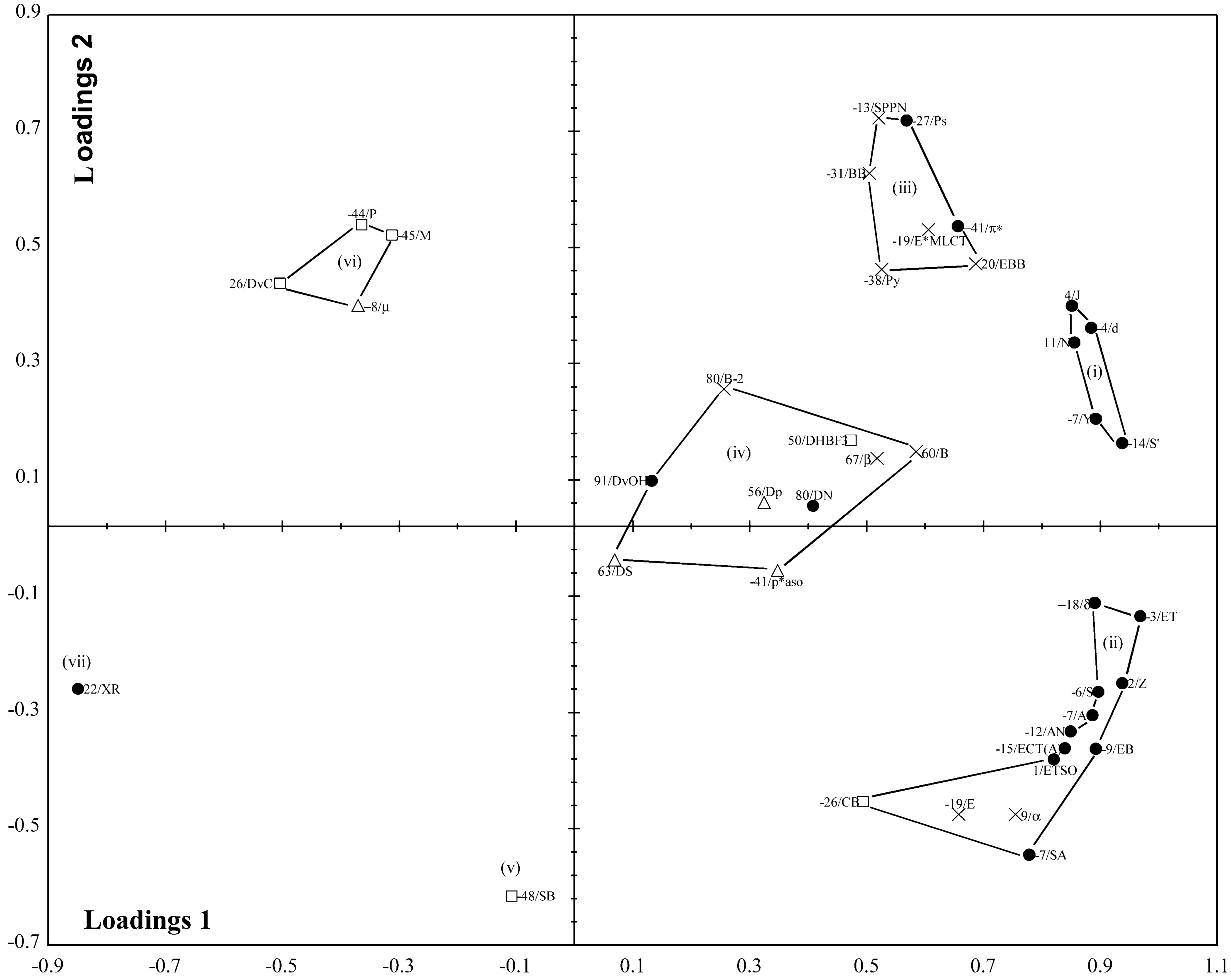

Figure 1. Loadings of the second PCA component plotted versus the loadings of the first component with the third component loading and scale classification given as labels to the data points. ●, ×, □, and △ represent $R \geq 90\%$, $80 \leq R < 90\%$, $70 \leq R < 80\%$, and $54 \leq R < 70\%$, respectively. (Reproduced with permission from *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 692. Copyright 1999 American Chemical Society.)

that the Kamlet-Taft β parameter is a good descriptor of the Gibbs free energies of hydrogen bonding.

A common hindrance to the application of all statistical methods, for the analysis of the dimensionality and the interrelation of the solvent scales, is the large number of missing values. PCA, for instance, requires a completely filled data matrix. Several methods can be used to deal with this problem. The simplest would be to exclude all scales and solvents for which there are insufficient data, but this approach leaves only a very small data matrix. It is preferable to predict the missing values, which can be done either using other highly intercorrelated scales (as was done by Palm and Palm) or from QSPR models built for each scale.

The last approach was chosen by the Florida-Tartu group,[235] who developed a complete data matrix for 40 scales by 40 solvents. To overcome the incompleteness of experimental data in the respective matrix, each scale was correlated with CODESSA descriptors to predict the missing scale values.[217] Their QSPR approach was already discussed under section 2.4. Following the CODESSA treatment, 40 scales involving 40 solvents were selected for the subsequent PCA analysis.

PCA allows the examination of a set of characteristics (variables) of a class of compounds (objects) to investigate the relations between them. It enables the identification of one, two, three, or more principal components (PCs) derived from the characteristics for the compounds examined. These components have defined values for each of the compounds (t_{1i}, t_{2i}, and t_{3i}, the “scores”) and are taken in certain proportions (p_{1k}, p_{2k}, p_{3k}, etc., the “loadings”) for each type of characteristic. Graphical representations of these values, the “scores” plot for the compounds and the “loadings” plot for the characteristics, provide pictures that allow the recognition of systematic patterns that are otherwise difficult to deduce from the original data matrix.

On the basis of the full 40 × 40 matrix, it was found[235] that most of the variation (>74%) in the data was described by just three principal components, whereas six components account for 90% of the variance. The loadings of the first three components divide the scales into seven distinct groups (Figure 1). Those groups are characterized as follows:[235]

(i) The five scales *J*, *S′*, *d*, *Y*, and *N* have large positive loadings (0.85−0.94) for the first component, small positive loadings (0.16−0.40) for the second component, and small loadings (−0.14 to 0.11) for the third component. These scales depend heavily on the solvent dielectric constant.

(ii) The 13 scales E_T, S, $E_{CT(A)}$, AN, A, E_B, Z, E, E_T^{SO}, SA, α, γ, and C_B have large positive loadings (0.49−0.97) for the first component, small to medium negative loadings (−0.11 to −0.55) for the second component, and relatively small loadings (−0.48 to 0.02) for the third component. Most of these scales are highly influenced by the solvent stabilization of charge transfer in the UV-vis absorption spectral maximum of large and highly polarized conjugated systems. According to the findings from the CODESSA treatment, these scales reflect mainly the acidic and electrophilic properties of solvents.

(iii) The seven scales BB, P_S, π^*, P_y, E^*_{MLCT}, E_{BB}, and SPP^N display medium to large positive loadings for the first (0.51−0.69) and second components (0.46−0.72) and small loadings (−0.41 to 0.20) for the third component. Most of these scales measure the ability of the solvent to change a UV absorption maximum, but unlike group ii these scales account more for nonspecific solvent dipole effects.

(iv) The nine scales B-2, ΔH^0_{BF3}, D_S, D_N, D_π, π^*_{aso}, $\Delta\nu_{OH}$, B, and β show small to moderate positive loadings (0.07−0.59) for the first component, small loadings (−0.06 to 0.26) for the second component, and large positive loadings (0.50−0.91) for the third component (except for the loading of π^*_{aso}, which is −0.41). These scales reflect solvent basicity.

(v) Scale SB is unique with a small negative first component and medium negative second (−0.62) and third components (−0.48). The SB scale can be used to describe solvent basicity effects based on experimental evidence from UV-vis spectroscopy. Apparently, this scale includes some specific solvent influence not well understood.

(vi) The four scales P, M, μ, and $\Delta\nu_{Cl}$ have medium negative first components (−0.31 to −0.504), medium positive second components (0.40−0.54), and small to medium positive or negative third components (−0.45 to 0.26). These scales mainly reflect the solvent refractive index (polarizability) and describe the softness of solvents.

(vii) Scale χ_R has a large negative first component (−0.85), a small negative second component (−0.26), and a small positive third component (0.22). This scale is based on the transition energy of merocyanine dyes.

Significantly, 34 of the 40 scales used in the PCA treatment[235] are concentrated into four major groups, i−iv. This is the same dimensionality of solvent effects as was suggested in 1972 by Koppel and Palm[9] on the basis of their classic analysis of the experimental data. Thus, these 34 results support their observation. However, the remaining six scales of groups v−vii deviate significantly in the PCA loadings.

Notably, as a result of the PCA treatment of the 40 × 40 matrix,[235] the solvents also showed clear clustering into five groups:

(i) Formamide has a very large positive score (2.02) for the first component and a medium positive score (0.59) and a small negative score (−0.26) for the second and third components, respectively. It is highly polar and can form both intermolecular and intramolecular hydrogen bonds, which distinguishes it from the solvents in group iii.

(ii) The nine hydroxylic solvents have moderate to large positive scores (water 3.14, others 0.32−1.36) for the first component and moderate to large negative scores (water −2.69, others −0.45 to −1.15) for the second component, together with variable scores (−1.39 to 1.01) for the third component. The very high first- and second-component scores separate water from the alcohols. The solvents of this group are all highly polar protic solvents, and all form strong hydrogen bonds.

(iii) The 12 dipolar aprotic solvents, which are strong H-bond acceptors but not donors, have small negative to medium positive scores (−0.09 to 0.68) for the first component, medium to large positive scores for the second component (0.48−1.80), and highly variable scores (−1.45 to 0.97) for the third component.

(iv) The ethers, esters, amine, alkyl halides, and five aromatic-ring-containing solvents have small to large negative scores (−0.32 to −1.21) for the first component, moderate negative to moderate positive scores (−0.61 to 0.34) for the second component, and very variable scores (−1.85 to 2.92) for the third component. These solvents possess polarity notably smaller than the solvents in groups ii and iii, but notably larger than those in group v.

(v) *n*-Hexane, cyclohexane, and carbon tetrachloride are distinct from other solvents with large negative scores for the first (−1.45 to −1.72) and second components (−1.25 to −1.69) and medium positive (0.32−0.41) or large negative scores (−2.25) for the third component. These three solvents are all apolar.

The PCA score grouping directly reflects the chemical nature of the solvents. Specifically, the solvents from the set of 40 fall into six distinct groups representing solvent classes from highly polar protic solvents (acetic acid and water) to apolar alkanes (*n*-hexane).

PCA and multivariate methods have both their advantages and weaknesses. Principal components have the built-in advantage of being mutually orthogonal, as compared to the sometimes highly intercorrelated nature of solvent scales. The most fundamental shortcoming of principal components is their lack of physicochemical correspondence to any theoretically derived property; the loadings are purely mathematical entities. The same can be said about purified solvent parameters that are obtained by subtracting the parts described by other parameters.

Finally, it is quite possible that all of the various physicochemical aspects of solvent-solute interaction are NOT orthogonal. Thus, acidity and electron pair donor properties likely depend on dipolarity and polarizability. Thus, residual descriptors could be very refined but lack any commonly understood names. Possibly we have to choose between orthogonality and good meaningful physicochemical parameters. To describe meaningfully separate types of interaction, one should use carefully chosen solvent parameters, whereas if the best overall fit and dimensionality are important, one should stick to orthogonal principal components or residual descriptors.

It is important to note that in most cases all treatments reveal high intercorrelation among various acidity (hydrogen-bond donor) scales. Reasonably distinct groups of scales are made up of nonspecific dipolarity, polarizability, and dielectric constant based scales. Basicity (hydrogen-bond acceptor) scales appear to have much larger variety, apparently due to the softness-hardness factor and the somewhat specific nature of electron donor sites. All of the treatments also appear to point in the same direction: although very many solvent polarity scales are highly interrelated and most of the scales can be grouped into some five large families, the whole variance in solvent-dependent processes cannot be accounted for using even as many as 9 or 10 parameters.

4. Summary and Future Work

As described above, major efforts have been made to develop quantitative scales and models to describe the solvent effects on chemical reactivity and physical properties of compounds in condensed media. It is essential to distinguish between two objectives that trigger those studies but that may lead to contradictory goals or conclusions from the research carried out. On the one hand, from the utilitarian point of view, it would be ideal to find a universal set of parameters that enable the quantitative prediction of the effects of solvent on as wide as possible a selection of physical, chemical, biological, and technological processes of solvents, and, on the other hand, it would be important to understand thoroughly the relationship between the different solvent parameters and the physical interactions between solute and solvent molecules. It is not obvious that the “best” set of parameters in the statistical sense would be the best to differentiate between individual physical interactions between solute and solvent.

Of course, most empirical solvent effect scales have been developed proceeding from some theoretical concepts about the intermolecular interactions in condensed media. In other words, the scales based on certain macroscopic experimental data are often related to individual, physically distinct mechanisms of solvation at the microscopic molecular level. Unfortunately, different experimentally observable chemical and physical processes are influenced, as a rule, simultaneously by several solute-solvent interactions in solution. The different mechanisms of interaction have, in general, a different relative importance in their influence on different experimental molecular properties in solution; thus, such “mixed” empirical solvent effect scales cannot be expected to be universally applicable. In addition, the cooperative effects (e.g., the restrictions to the polarization due to hydrogen bonding) may bring up nonlinear dependencies of observable properties from solvent scales defined using some standard process or measurable quantity. One possible formal way to account for such nonlinearities would be the use of so-called “cross-terms” in the model development, introduced as the products of different scales. Notably, this approach has been used very rarely in the description of solvent effects, but it could have some value if a formal model for a wide spectrum of solvents is aimed for.

Another approach that would possibly help to elucidate further the content of different empirical solvent effect scales would be the PCA and QSPR treatment of these scales together with various theoretically calculated contributions to the free energy of solvation. Those contributions correspond conventionally to the electrostatic and dispersion interactions between the molecules in condensed media and involve also the effects related to the cavity formation and solvent reorganization.[236−241] Such analysis would be particularly useful for the attempts to develop new, universally applicable theoretical descriptors for solvent effects.

Last but not least, it must be emphasized the present solvent polarity scales are mostly derived for pure solvents. However, a large part of chemistry and many natural processes are carried out in mixtures of solvents. Therefore, it would be of much practical importance to extend the solvent scales and the corresponding QSPR models to multicomponent systems.

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