

## QSPR Treatment of Solvent Scales

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The results of the quantitative structure–property relationship (QSPR) analysis of 45 different solvent scales and 350 solvents using the CODESSA program are presented. The QSPR models for each of the scales are constructed using only theoretical descriptors. The high quality of the models (32 of the 45 give  $R^2 > 0.90$ , only two have  $R^2 < 0.82$ ) enables direct calculation of predicted values for any scale for any previously unmeasured solvent. The descriptors involved are shown to be in good agreement with the physical concepts invoked by the original authors of the scales.

### INTRODUCTION

The use of solvents is fundamental to the practice of chemistry. The prediction of the influence of a change in solvent and the choice of an appropriate solvent can be anything but trivial. The polarity and other properties of solvents are not easily defined using exact physical characteristics. Many solvent scales were therefore developed to assist chemists in their understanding of solvent properties and in their choice of solvent. These scales are based on diverse physico-chemical phenomena including reaction rates, solvatochromic effects, and reaction enthalpies, among others. Frequently the actual mechanism of the solvent influence on a physical or chemical process is unclear. The same is often true of the individual solvent scales. Several analyses of solvent scales together with reviews and discussions on the subject have been published.<sup>1</sup>

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 ( $\pi^*$ ,<sup>1f</sup>  $S'^2$ ,<sup>2</sup>  $SPP^N$ <sup>1i</sup>). Many scales are limited to a specific range of solvent polarity or other property due to restrictions in the methodology of their measurement: for example, 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.

The present study collects a representative set of different solvent scales, develops QSPR (quantitative structure–property relationship) models using theoretically developed molecular descriptors for each of them, and undertakes a comparison of the QSPR equations of the different scales to elucidate their similarities and differences. The comparison and detailed analysis of the descriptors that describe each scale provides insight into the mechanisms of the influence of solvents on various processes and criteria for the choice of the solvent scale most useful for a specific purpose.

### DATA SET

Individual experimental solvent scales were taken from the literature. The scales that have been proposed in the literature vary greatly in the number of solvents included, from less than 20 to several hundreds. The 45 scales used in our study contain data for a total of 350 different solvents; the 65 solvents given in our tables are each present in 10 or more of these 45 individual scales.

Table 1 presents the 45 different solvent scales that were selected for the present QSPR study, each with 20 or more data points. Many of these 45 solvent scales are widely used (e.g., DN, AN,  $\alpha$ ,  $\beta$ ,  $E_T(30)$ ). Table 1 lists references to the scales and a brief description of the phenomena selected by the original authors to create each scale. The scales in Table 1 are divided into groups according to the physical process on which they depend. Within each group, the scales are listed in descending order of the number of solvents they include from our set of 65 solvents. The second column contains our own designated symbol for each solvent scale. To avoid duplicates, a number of the symbols listed had to be changed from those proposed by the original authors (see footnotes to Table 1). Columns three and four of Table 1 give the authors of each scale and a short description of the method by which the scales were originally defined and measured. The references in the last column denote the literature sources from which the data used in the present study were taken.

Table 2 lists the 65 solvents that are included in at least 10 of the 45 experimental solvent scales of Table 1 in descending order of the number of scales in which they are represented. Some scales are more appropriate for more polar solvents (such as  $E_T$ , DN, Z), and many probes cannot be used in all solvents (because of chemical reaction, solubility problems, etc.). All these aspects affect the number of data points for any particular solvent.

Table 3 in the Supporting Information lists the 65 solvents in the same order as Table 2. However, Table 3 also gives for each solvent the available experimental values of each of the 45 scales used in our study. Some authors have normalized their scales, whereas others have not. We give

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**Table 1.** Solvent Scales Used in the Study

no.	scale	author of scale	physical background	ref <sup>a</sup>
Spectral Scales: Based on Charge Transfer, Electronic Excitation, etc. Processes				
1	E <sub>T</sub>	Dimroth and Reichardt	electronic transition energy of pyridinium <i>N</i> -phenolate betaine dye	14
2	SA	Catalan and Diaz	vis spectra of <i>o</i> - <i>t</i> -butylstilbazolium betaine dye and its di- <i>t</i> -butyl homomorph	15
3	P <sub>s</sub>	Freed et al.	bathochromic UV/vis spectra shifts of $\lambda_{\max}$ of ( $\alpha$ -perfluoroheptyl- $\beta$ , $\beta$ -dicyanovinyl)aminostyrenes	16
4	B	Koppel and Palm	(basicity) from stretching frequency of CH <sub>3</sub> OD in different solvents	1a, 17
5	B-2 <sup>b</sup>	Koppel and Paju	acid–base hydrogen bond formation induced shifts of phenol OH group stretching frequency	18
6	SB	Catalan et al.	UV/vis spectra of 5-nitroindoline and 1-Me-5-nitroindoline	19
7	$\alpha$	Kamlet and Taft	various probes (longest wavelength absorption)	1g, 20
8	$\beta$	Kamlet and Taft	various probes (longest wavelength absorption)	1g, 21
9	P <sub>y</sub>	Dong and Winnik	vibronic fine structure. of pyrene fluorescence spectra	22
10	AN	Gutmann and Mayer	<sup>31</sup> P NMR of triethylphosphine oxide in different solvents	1g, 23
11	E <sub>B</sub>	Janowski et al.	N $\rightarrow$ $\pi^*$ transition of 2,2,6,6-tetramethylpiperidine- <i>N</i> -oxyl	24
12	D <sub>S</sub>	Persson	(for soft acceptors) Raman/IR stretching freq of Hg <sub>2</sub> Br <sub>2</sub> in gas phase and solutions	25
13	Z	Kosower	transition energy for the CT absorption of 1-ethyl-4 methoxycarbonylpyridinium iodide	26
14	$\Delta\nu_{\text{OH}}$	Laurence et al.	IR frequency shifts of phenol hydroxyl group	27
15	$\pi^*$	Kamlet	shifts of $\pi \rightarrow \pi^*$ absorption band of a set of nitroaromatic compounds	28
16	$\Delta\nu_{\text{Cl}}$	Laurence et al.	IR stretching of iodine cyanide C–I bonds	27
17	E* <sub>MLCT</sub>	Manuta and Lees	electronic spectra of metal to ligand charge transfer of W(CO) <sub>4</sub> (2,2'-bipyridine)	29
18	SPP <sup>N</sup>	Paéz et al.	UV/vis spectra of 2-dimethylamino-7-nitrofluorene and 2-flouro-7-nitrofluorene	1i
19	$\chi_{\text{R}}$	Brooker	transition energy of merocyanine dye	30
20	E <sub>T</sub> <sup>SO</sup>	Walter and Bauer	UV/vis spectra of <i>N,N</i> -(dimethyl)thiobenzamide- <i>S</i> -oxide	31
21	E <sub>CT</sub> ( $\pi$ )	Kaim et al.	CT spectra of W(CO) <sub>5</sub> and Cr(CO) <sub>5</sub> complexes with TCNE	32
22	$\pi^*_{\text{aso}}$	Buncel and Rajagopal	bathochromic shifts of 6 azo merocyanine dyes	33
23	E <sub>CT</sub> (A)	Davis	UV CT absorption maximums of tetra- <i>n</i> -hexylammonium iodide trinitrobenzene	34
24	XX <sup>c</sup>	David and Hallam	vibrational frequencies of SO <sub>2</sub>	35
25	$\Phi$	Dubois	position of the $n \rightarrow \pi^*$ transition of a set of ketones	36
Nonspectral Scales (Thermodynamic, Optical, etc.)				
26	DN	Gutmann and Wychera	$\Delta H$ of reaction between SbCl <sub>5</sub> and the solvent	37
27	d		dielectric constant	1d
28	$\Delta H^0_{\text{BF}_3}$	Maria and Gal	enthalpy of complexation of solvents with BF <sub>3</sub> in dichloromethane	38
29	E <sub>BB</sub> <sup>d</sup>	Drago	(susceptibility to electrostatic interaction of a base) statistical from $\Delta H$ data of different bases and acids	39
30	C <sub>B</sub>	Drago	(susceptibility to covalent interaction of a base) statistical from $\Delta H$ data of different bases and acids	39
31	D $\pi$	Oshima et al.	second-order rate constant of the reaction of DDM and TCNE	40
32	$\delta$	Hildebrand	square root of cohesive pressure	1b
33	$\mu$	Marcus	$\Delta G$ of the transfer of Ag <sup>+</sup> , Na <sup>+</sup> , and K <sup>+</sup> ions from water to solvent	41
34	X	Fletcher et al.	absorption of solution	42
35	D <sub>H</sub>	Persson	(for hard acceptors) $\Delta G$ of the transfer of Na <sup>+</sup> from solvent to reference solvent (1,2-dichloroethane)	25
Combined Scales: Derived from Other Parameters or from Statistical Analysis of Different Measurements				
36	J	Kirkwood and David	expression of dielectric constant	1d
37	M	McRae	expression of refractive index	1d
38	E	Koppel and Palm	(acidity) derived from E <sub>T</sub> and P and Y	1a, 17
39	P	Koppel and Palm	(polarizability) expression of refractive index	1a, 17
40	Y	Koppel and Palm	(polarity) expression of dielectric constant	1a, 17
41	N	McRae	combination of M and P	1d
42	A	Swain et al.	free energy changes in 77 reactions (data from electronic, IR, ESR, NMR spectra; kinetic and equilibrium measurements)	43
43	BB <sup>b</sup>	Swain et al.	as above	43
44	S	Brownstein	derived from Kosower Z values, uses <i>R</i> for process sensitivity	44
45	S'	Drago	statistical, $\Delta\chi = \text{PS}' + \text{W}$ (30 probes, 31 solvents, >300 shifts)	45

<sup>a</sup> Reference to where the data was taken from, not necessarily the same as the original reference to the scale. <sup>b</sup> As three parameters share the same name, the original "B" of Swain et al. is replaced by "BB" and Koppel's newer B scale is changed to be "B-2". <sup>c</sup> In order to avoid duplicate names, the "X" scale of David is marked as "XX". <sup>d</sup> In order to avoid duplicate names, Drago's newer "E<sub>B</sub>" scale is marked "E<sub>BB</sub>".

the scales unmodified as they appear in the literature but have eliminated duplicates. In the case of E<sub>T</sub>(30), for instance, both normalized and non-normalized scales are available, we have chosen the non-normalized scale.

In order 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  $\log X$ . We selected the best correlation as indicated in the scale symbols in Table 4. For example, scales Y, SB, d, J, BB, C<sub>B</sub>, E\*<sub>MLCT</sub>,

D $\pi$ , and SPP<sup>N</sup> were found to be best correlated in Y<sup>2</sup>, SB<sup>-2</sup>,  $\log(d)$ , J<sup>2</sup>, BB<sup>3</sup>, C<sub>B</sub><sup>-2</sup>, E\*<sub>MLCT</sub><sup>3</sup>, D $\pi$ <sup>3</sup>, and (SPP<sup>N</sup>)<sup>3</sup>, respectively.

## METHODOLOGY

The geometrical structures of the solvent molecules were optimized using the AM1<sup>3</sup> method within the MOPAC<sup>4</sup> program package. The geometry and other information from the output of quantum chemical calculations were inserted

**Table 2.** Sixty-five Solvents Common to 10 or More Scales of Table 1

no.	solvent name	no. of scales	no.	solvent name	no. of scales	no.	solvent name	no. of scales
1	acetone	43	23	toluene	31	45	aniline	17
2	acetonitrile	43	24	diethyl ether	30	46	cyclohexanol	17
3	benzene	40	25	<i>tert</i> -butanol	30	47	benzyl alcohol	16
4	ethanol	39	26	1-propanol	29	48	<i>N</i> -methylformamide	16
5	methanol	39	27	1,2-dichloroethane	29	49	<i>o</i> -dichlorobenzene	16
6	<i>N,N</i> -dimethylformamide	38	28	bromobenzene	28	50	piperidine	15
7	THF	37	29	formamide	28	51	carbon disulfide	15
8	benzonitrile	36	30	<i>n</i> -hexane	28	52	propylene carbonate	15
9	dimethyl sulfoxide	36	31	cyclohexane	27	53	1-pentanol	15
10	chloroform	35	32	cyclohexanone	27	54	trimethyl phosphate	14
11	dichloromethane	35	33	water	27	55	tetramethylene sulfone	14
12	ethyl acetate	35	34	1,2-ethanediol	26	56	1,3,5-trimethylbenzene	14
13	nitromethane	35	35	acetic acid	26	57	2-butanol	14
14	1,4-dioxane	34	36	2-butanone	23	58	fluorobenzene	13
15	1-butanol	34	37	anisole	22	59	1-octanol	13
16	<i>N,N</i> -dimethylacetamide	34	38	acetophenone	20	60	2-methyl-1-propanol	13
17	pyridine	33	39	methyl acetate	20	61	<i>N</i> -methylacetamide	11
18	2-propanol	32	40	triethylamine	20	62	<i>n</i> -heptane	11
19	chlorobenzene	32	41	diisopropyl ether	18	63	1-hexanol	11
20	nitrobenzene	32	42	1,2-dimethoxyethane	18	64	quinoline	10
21	carbon tetrachloride	31	43	HMPA	18	65	1,1-dichloroethane	10
22	di- <i>n</i> -butylether	31	44	1,1,3,3-tetramethylurea	17			

into the CODESSA<sup>5</sup> program, and descriptors were calculated. All these descriptors are derived solely from molecular structure and do not require experimental data to be calculated. The CODESSA program was then used to find the best multilinear equations with 2, 3, or 4 descriptors depending on the size of the data set of each scale. Both *Heuristic* and *Best Multi-Linear* correlation algorithms available in the CODESSA were used. The methodology of the QSPR treatment used is described elsewhere.<sup>6</sup> The CODESSA program has already been successfully applied to correlate molecular structure with various properties including melting points,<sup>7</sup> response factors,<sup>8</sup> critical micelle concentrations,<sup>9</sup> aqueous solubility of gases,<sup>10</sup> and glass transition temperatures of polymers.<sup>11</sup>

## RESULTS AND DISCUSSION

Table 4 gives the results of the QSPR treatment of the solvent scales. The first two columns are the same as in Table 1, and the third column shows the number of experimental data points used for each scale. The QSPR equation given in the fourth column is in the form of coefficients and descriptors, together with the *t*-test values. The value of the coefficient cannot be treated as an indicator of the importance of the descriptor in an equation as the absolute numeric values of the descriptors vary in a large range (the descriptors are not normalized), thus, the *t*-test value for each descriptor has been used instead for the purpose. The last three columns of Table 4 show the statistical parameters of the QSPR equations: the squares of the correlation coefficients ( $R^2$ ), the squares of the standard deviations ( $s^2$ ), and the squares of cross-validated correlation coefficients ( $R_{cv}^2$ ). Most of the developed QSPR equations have a satisfactory correlation coefficient; 32 out of 45 have  $R^2$  higher than 0.90, and only two have  $R^2 < 0.82$ .

The equations in Table 4 can be used for all of the 45 solvent scales listed in Table 3 to predict the solvent scale value for any solvent for which no experimental value is available. Let us consider the DN scale and the missing solvent *N,N*-dimethylacetamide as an example. In order to

predict the DN for the solvent, we need to calculate the descriptor values for the molecule and insert the values into the QSPR equation:  $DN_{(N,N\text{-dimethylacetamide})} = -12.6$  (intercept)  $- [151 \times -0.107$  (max partial charge for a N atom)]  $+ [67.1 \times 0.169$  (polarity parameter  $Q_{\max}-Q_{\min}$ )]  $+ [10.0 \times 0.425$  (total hybridization component of the molecular dipole)]  $+ [16.0 \times 0.738$  (PSA of H atoms)]  $= 31.0$

The result is comparable with the DN value for *N,N*-dimethylformamide of 26.6 and that for *N*-methylacetamide of 27.8. Taking another basicity scale, the B-2 scale, as a reference we see a similar tendency with *N,N*-dimethylacetamide having a higher value than *N,N*-dimethylformamide. The good agreement proves that although the  $R^2$  value of the DN scale is not very high, the correlation still allows predictions with reasonable accuracy.

Furthermore, these models allow the physical mechanisms behind each scale to be assessed according to the occurrence of the different descriptors which model the dependence of the process in question in the form of specific structural elements. The theoretical background of each descriptor has been explained elsewhere.<sup>5,12</sup>

The QSPR equations for the 45 scales contain altogether 118 different descriptors. Some of these descriptors are very similar, e.g., they can depend on the same property and differ only in their calculation methods, or they may derive from both semi-empirical and empirical (Zefirov's) methods of calculation for the same property. Therefore, the number of independent descriptors is actually less than 118, but no attempt was made to reduce the number of descriptors by substitution of one descriptor for another similar one. The intercorrelation of the descriptors is discussed later. The descriptors are unevenly used in the equations: the total dipole of the molecule is used eight times; the maximum partial charge for a N atom, five times; LUMO energy and image of the Onsager-Kirkwood solvation energy, four times. Four descriptors are used three times; 20 descriptors, twice; and 90 descriptors, just once.

The names of the descriptors that were used in the equations of Table 4 are listed in Table 5; they can be divided

Table 4. QSPR Models of the Solvent Scales

	scale	size <sup>a</sup>	intercept	coef. 1	D1 <sup>b</sup>	t-test	coef. 2	D2 <sup>b</sup>	t-test	coef. 3	D3 <sup>b</sup>	t-test	coef. 4	D4 <sup>b</sup>	t-test	R <sup>2</sup> <sup>c</sup>	s <sup>2</sup> <sup>c</sup>	R <sup>2</sup> <sub>cv</sub> <sup>c</sup>
1	E <sub>T</sub>	246	29.1	8.62	c16	14.0	3.90	c10	-12.4	2.60	h14	9.69	1.80	c09	-5.12	0.880 <sup>d</sup>	4.76	0.870
2	DN	96	-12.6	-151	c17	-10.9	67.1	c27	8.56	10.0	e18	6.93	16.0	p05	5.96	0.837	26.8	0.816
3	SA	92	-634	4350	h03	32.8	28800	e11	7.73	-337	e04	-6.98				0.926	29100	0.905
4	P <sub>s</sub>	71	0.148	1.04	e17	11.2	0.220	c06	9.81	-10.2	p04	-7.50	6.65	p03	6.39	0.832	0.861	0.802
5	B	62	45.8	-188	c15	-15.6	-7.45	b04	-9.92	49.3	g05	7.71	6.12	e03	4.56	0.903	151	0.892
6	E	62	135	1.58	h15	31.4	-1.25	t08	-7.66	-33.4	e08	-6.27				0.953	0.854	0.946
7	Y <sup>2</sup>	62	0.0720	0.0565	e17	28.0	0.00700	h13	19.3	-0.0268	c03	-8.45	-0.00550	e15	-5.80	0.949	0.000200	0.932
8	P	62	0.305	-0.00120	c05	-16.2	0.0127	e01	13.6	0.0210	t09	11.5	-0.0277	c15	-5.55	0.955	0.00	0.932
9	SB <sup>-2</sup>	60	491	17.5	b06	78.8	-5.84	b05	-9.06	822	c22	6.07	22.5	e03	4.73	0.992	1780	0.975
10	B <sup>-2</sup>	60	2.70	-4250	c17	-20.2	-1020	c18	-14.1	-6660	e06	-12.4	3790	b09	5.64	0.933	1290	0.913
11	α	57	17.1	0.0102	b13	8.33	0.0212	b10	4.02	0.00580	h16	3.25	-0.0677	t10	-3.14	0.919	0.0100	0.903
12	β	57	0.0560	0.451	e18	14.8	0.00140	b12	12.2	19.0	c19	11.0	0.0166	h01	6.63	0.901	0.0100	0.886
13	log(d)	55	0.569	0.287	e17	17.7	99.5	h12	9.04	-0.0833	t10	-3.34	-2.99	e07	-2.41	0.910	0.0249	0.891
14	J <sup>2</sup>	54	-0.159	0.149	e17	16.4	4.58	h10	13.1	-0.231	c13	-3.54	0.157	e05	2.44	0.922	0.00710	0.905
15	M	54	0.260	0.000291	c26	10.1	0.998	e01	8.47	2.29	c24	5.85	0.133	g09	5.73	0.913	0.000100	0.884
16	N	54	0.0340	0.118	e17	16.4	2.72	h11	8.53	0.278	c29	5.28	-0.0365	c02	-4.13	0.915	0.00530	0.894
17	P <sub>y</sub>	51	1.48	0.0654	p07	12.0	2.82	o01	9.73	-0.802	c11	-7.64	-2.96	h06	-6.12	0.875	0.0173	0.828
18	AN	50	-5.85	0.238	b08	9.74	-53.6	c16	-7.80	47.5	h02	6.55	31.6	t05	6.52	0.956	15.0	0.937
19	A	50	-0.157	0.00690	b08	20.5	0.625	t04	7.76	0.0139	b10	5.33	-1.30	c10	-4.71	0.957	0.00340	0.944
20	BB <sup>3</sup>	50	0.577	0.0348	c23	7.02	-4.68	c17	-6.35	-0.660	b01	-4.53	-1.11	p06	-3.22	0.755	0.0444	0.672
21	ΔH <sup>o</sup> BF <sub>3</sub>	50	1.36	-2.22	c17	-13.8	10.0	c25	8.76	-0.0449	g07	-8.07	1.47	h18	6.96	0.930	0.00240	0.910
22	E <sub>B</sub>	48	-0.0920	0.0213	b16	20.0	0.630	t04	16.8	3.80	h04	11.5				0.978	0.00100	0.971
23	Z	45	58.9	0.855	b16	6.86	3.68	o01	5.44	4.96	-h19	5.11	0.160	h17	4.02	0.920	8.54	0.896
24	D <sub>S</sub>	45	31.9	-167	c17	-11.5	243	e13	9.37	-9.32	b03	-7.00	-209	c21	-3.71	0.884	20.0	0.859
25	Δν <sub>OH</sub>	42	369	-1850	c20	-8.39	-456	c07	-6.08	-7230	b03	-4.13	96.2	e18	4.02	0.867	3760	0.830
26	π*	38	23.6	28.2	c12	11.0	-0.181	e03	10.9	0.130	e17	7.24	-0.208	g04	-5.04	0.900	0.0103	0.862
27	E <sub>BB</sub>	33	-0.408	0.348	e17	8.89	0.268	c28	8.25	-0.00550	c01	-4.51	0.0606	g02	3.88	0.816	0.0430	0.757
28	C <sub>B</sub> <sup>-2</sup>	33	4.34	2014	g06	129	-3.64	c29	-5.04	-0.256	t11	-3.29				0.999	0.439	0.997
29	Δν <sub>Cl</sub>	33	-1350	-399	c20	-14.4	205	p02	6.89	13.1	e09	6.27				0.906	56.1	0.878
30	S	32	-0.341	0.0172	c30	12.6	-0.0456	c32	-10.7	1.11	h08	8.78				0.964	0.000600	0.952
31	E* <sub>MLCT3</sub>	32	-0.0540	4.22	o01	20.6	-0.383	c08	-4.07	0.000400	b07	2.77				0.960	0.00370	0.945
32	D <sub>π</sub> <sup>3</sup>	32	0.102	-0.190	g07	-17.1	0.400	e19	5.05	-0.360	t06	-2.78				0.941	0.0548	0.917
33	(SPP <sup>N</sup> ) <sup>3</sup>	30	0.344	0.194	e17	13.7	-1.31	g08	-5.25	-0.00170	c33	-3.57				0.906	0.00300	0.865
34	δ	30	16.7	45.3	h05	18.2	33.4	o01	8.77	37.3	g09	3.92				0.924	4.39	0.912
35	μ	30	0.00780	-0.0126	p08	-14.1	4.73	p01	5.24	-0.0174	p07	-3.98				0.927	0.0105	0.893
36	χ <sub>R</sub>	29	43.8	-1.85	h19	-10.9	-0.205	c31	-7.41	5.53	g10	6.76				0.889	0.787	0.853
37	E <sub>T</sub> <sup>SO</sup>	29	78.7	0.0500	b15	11.6	5.83	t04	6.80	0.0777	h13	4.99				0.965	0.256	0.953
38	X	28	-0.115	-1.39	h11	-16.7	0.0269	e02	15.6	0.117	b11	9.53				0.963	0.00	0.953
39	E <sub>CT(π)</sub>	25	-0.0860	0.0381	c34	8.30	0.0423	h09	3.75	1.47	g01	3.73	0.00780	t07	-3.18	0.845	0.0163	0.757
40	S'	25	1.90	-8.76	c10	-10.8	2.58	h14	6.97	-0.234	t02	-4.38				0.936	0.0227	0.927
41	π* <sub>aso</sub>	23	2.91	-1.07	e10	-10.6	0.157	e17	9.60	-0.113	c03	-4.37				0.934	0.00720	0.898
42	E <sub>CT(A)</sub>	23	20.0	24.3	h05	9.97	3.60	t01	3.68	-1.16	b02	-2.44				0.923	0.348	0.875
43	D <sub>H</sub>	23	2.25	-43.1	c14	-6.53	-47.2	c15	-4.72	-2.83	b14	-3.76				0.837	51.4	0.729
44	XX	21	15.2	-18.7	e16	-9.81	6.82	t03	7.04	4.01	e14	6.69				0.890	2.77	0.801
45	Φ	20	0.0600	-3.84	c04	-18.9	0.0644	e03	12.3							0.958	0.00100	0.937

<sup>a</sup> The column shows the actual number of data points used for the QSPR analysis. <sup>b</sup> D1, D2, D3, and D4 stand for the different descriptors used in each model. <sup>c</sup> R<sup>2</sup> is the square of the correlation coefficient, s<sup>2</sup> is the square of the absolute error, R<sup>2</sup><sub>cv</sub> is the square of the cross-validated correlation coefficient. <sup>d</sup> R<sup>2</sup> = 0.880 was obtained using five descriptors (8.62 c16 + 2.60 h14 + 3.90 c10 + 1.80 c09 + 129 h07).



**Table 5.** Descriptors Used in the QSPR Models of the Solvent Scales

descriptor names		descriptor names	
Bonding Interactions			
b01	aver. bond order of a C atom	b09	max SIGMA-PI bond order
b02	max $\pi$ - $\pi$ bond order	b10	max total interaction for a H-N bond
b03	max bond order for a C atom	b11	min Coulombic interaction for a C-H bond
b04	max Coulombic interaction for a N-O bond	b12	min e-e repulsion of a C-O bond
b05	max e-n attraction for a C-H bond	b13	min e-e repulsion of a H-O bond
b06	max exchange energy for a C-Cl bond	b14	min exchange energy for C-S bond
b07	max n-n repulsion for a C-N bond	b15	mini n-n repulsion for a H-O bond
b08	max n-n repulsion for a H-O bond	b16	min total interaction for H-O bond
Partial Surface Areas			
p01	PSA-2 of C atoms	b05	PSA of H atoms
p02	PSA-2 of H atoms	p06	PSA of O atoms
p03	PSA of C atoms	p07	SA-2 of O atoms
p04	PSA of F atoms	p08	SA of S atoms
Geometrical/Constitutional			
g01	moment of inertia B	g06	principal moment of inertia B/number of atoms
g02	number of aromatic bonds	g07	relative molecular weight
g03	number of C atoms	g08	relative number of double bonds
g04	number of double bonds	g09	relative number of rings
g05	number of N atoms	g10	relative number of single bonds
Topological			
t01	aver. bonding inf. content (order2)	t07	compl. information content (order 2)
t02	aver. complementary inf. content (order 2)	t08	Kier & Hall index (order 2)
t03	aver. inf. content (order 1)	t09	Kier & Hall index (order 3)
t04	aver. struct. information content (order 0)	t10	Randic index (order 2)
t05	aver. struct. information content (order 1)	t11	structural information content (order 1)
t06	Balaban index		
Charge Distribution			
c01	1*BEETA polarizability	c18	max partial charge for a O atom
c02	CSA-2 of C atoms	c19	max partial charge for a S atom [Zef.]
c03	CSA-2 of N atoms	c20	min partial charge for a N atom [Zef.]
c04	difference of PCSAs	c21	min partial charge for a H atom [Zef.]
c05	DPSA-1 [Zef.]	c22	min partial charge Qmin [Zef.]
c06	DPSA-3 [Zef.]	c23	neg. charged CSA
c07	FNSA-1 [Semi]	c24	PCSA-2 of H atoms
c08	FNSA-2 [Semi]	c25	PCSA of H atoms
c09	FNSA-2 [Zef.]	c26	PNSA-1 [Zef.]
c10	FNSA-3 [Semi]	c27	polarity parameter (Qmax-Qmin)
c11	FPSA-1 [Semi]	c28	PPSA-3 [Zef.]
c12	FPSA-3 [Semi]	c29	RNCG [Zef.]
c13	max net atomic charge for a C atom	c30	RPCS [Zef.]
c14	max net atomic charge for a N atom	c31	RPCS [Semi]
c15	max net atomic charge for a O atom	c32	WNSA-3 [Zef.]
c16	max partial charge for a H atom [Zef.]	c33	WPSA-1 [Zef.]
c17	max partial charge for a N atom	c34	WPSA-2 [Zef.]
Electronic Properties			
e01	HOMO - 1 energy	e11	min electroph. react. index for a Cl atom
e02	HOMO energy	e12	min e-n attraction for a S atom
e03	LUMO energy	e13	min nucleoph. react. index for a S atom
e04	max antibonding contribution of a MO	e14	topogr. electronic index (all bonds) [Semi]
e05	max atomic orbital electron population	e15	topogr. electronic index (all pairs) [Semi]
e06	max nucleoph. react. index for a N atom	e16	topogr. electronic index (all pairs) [Semi]
e07	max nucleoph. react. index for a O atom	e17	total dipole of the molecule
e08	max valency of a C atom	e18	total hybridization component of the molecular dipole
e09	min atomic state energy for a C atom	e19	total molecular electro. interaction/number of atoms
e10	min e-e repulsion of a H atom		
Hydrogen Bonding			
h01	count of H donor sites [Zef.]	h11	HACA-2/TMSA [Semi]
h02	FHASA (HASA/TMSA) [Semi]	h12	HACA-2/TMSA [Zef.]
h03	FHBSA [Semi]	h13	HACA [Semi]
h04	FHDCA [Semi]	h14	HASA-1/TMSA [Zef.]
h05	FHDSA [Semi]	h15	HDCA [Semi]
h06	HA dependent HDCA-2/SQRT(TMSA)[*Semi*]	h16	HDSA [Semi]
h07	HA dependent HDCA-1/TMSA [Semi]	h17	new H-acceptor CPSPA
h08	HA dependent HDCA-2/SQRT(TMSA) [Semi]	h18	new H-acceptor FCPSA
h09	HACA-2/SQRT(TMSA) [Semi]	h19	RT:1 HACA2
h10	HACA-2/SQRT(TMSA) [Zef.]		
Other			
o01	image of the Onsager-Kirkwood solvation energy		

into eight groups. The largest groups based on the number of individual descriptors inside each are those related to charge distribution (34 descriptors), hydrogen bonding (19 descriptors), and general electronic properties (19 descriptors). Descriptors describing the geometry and constitution (10) and topology (11) of the solvent molecule are also important. If the total number of occurrences rather than the number of different descriptors is considered, then the largest groups are the charge distribution related descriptors (used 47 times), electronic properties (32), hydrogen bonding descriptors (25) and bonding interactions (20), and topological indices (14). The descriptor groups relating to partial surface area, geometrical, constitutional, and other properties were each used less than 10 times. Of the equations, 22 include hydrogen bonding related descriptors (19 different descriptors). The  $E_T$  and  $Z$  scales are highly dependent on hydrogen bonding, and both have two hydrogen bonding related descriptors. Atom-specific descriptors (PSA of F atoms, SA of S atoms, relative number of rings, etc.) have non-zero values for only very few solvents. The inclusion of such descriptors correlates specifically some of the outlying solvents.

The group of descriptors related to charge distribution describes the positively and negatively charged surface areas of the solvents (both the absolute values and those relative to the total surface area) and also atom-specific partial charges (miscellaneous SA descriptors). These are calculated from both empirical<sup>12c</sup> (denoted as Zef. for Zefirov) and semi-empirical quantum-chemical charge distributions (denoted as Semi). Included in this group are the most negative and most positive partial charges on given types of atoms. The importance of these descriptors is understandable, as charge distribution is one of the key properties that determines the solute-solvent interactions in liquid media.

The descriptors from the hydrogen bonding group are directly dependent on the hydrogen bonding donor or acceptor ability of the molecule. Various descriptors of this type account for the partial surface areas of the molecule capable of donor and acceptor binding (miscellaneous SA) and specifically charged areas (CA).

A quite diverse group of descriptors involves general electronic properties: it ranges from simple HOMO and LUMO energies to topographical electronic indices. Most of these descriptors are calculated using the results of the semi-empirical AM1 method. Among these, descriptors e11 and e12 both refer to the electronic state of the carbon atom. Some other descriptors from this group reflect the specific nature the atom species involved.

The group of descriptors reflecting bonding interactions (16 in all) is calculated from the semi-empirical electronic wave functions and interatomic distances. The partial surface areas (eight descriptors) are calculated from Van der Waals radii and are essentially self-explanatory: the notations PSA and PSA-2 refer to slightly different calculation algorithms of the surface areas. The group of topological descriptors (11) gives information about branching and connectivity of the molecule. The group of geometrical and constitutional descriptors (10) is also self-explanatory.

Although some polarity scales (electrophilicity, polarizability, etc.) are dependent on just one well-defined property of the solvent, most reflect diverse effects.<sup>1b</sup> Correspondingly, most of the QSPR models now derived comprise a diverse

set of descriptors, rather than depending on one type of parameter. Nevertheless, a few scales do seem to rely mostly on one type of effect; for example, the model for the  $\mu$  scale uses only partial surface area descriptors, which is in accordance with the definition of this scale in as much as the transfer energy is primarily dependent on the partial surface areas of various specific atoms in the solvent molecule. In the  $\mu$  scale, no electron or charge related descriptors were involved.

The models for (i) the well-known  $E_T$  scale, (ii) susceptibility of bases to electrostatic interactions (Drago's  $E_B$  scale, denoted  $E_{BB}$  in our tables), (iii) the cation solvating tendency scale B of Swain ( $E_{BB}$  in our tables), and (iv) the S scale of Brownstein (derived from spectroscopic values of the Z scale by Kosower) each use only charge distribution related descriptors (the hydrogen bonding descriptors are very close in their nature to other charge distribution descriptors). This suggests that the size and shape of the solvent molecule are not crucial in the determination of these four scales, for which the electronic structure and the existence of highly electronegative atoms are of more significance. Accordingly, it is well known that  $E_T$  is a good measure of solvent hydrogen bonding ability,<sup>1d</sup> a property that is strongly dependent on charge distribution.

The descriptors in each correlation model are given in Table 5 in the order of the (absolute)  $t$ -test values. In this way, the most significant descriptors for each model are in the D1 column (Table 5). If two scales have the same most significant descriptors, it follows the two scales should depend predominantly on the same chemical parameter or effect. For example, e17 (total dipole of the molecule) is the most significant descriptor for each of the seven scales:  $P_S$ ,  $Y^2$ ,  $\log(d)$ ,  $J^2$ ,  $(SPP^N)^3$ ,  $E_{BB}$ , and  $N$ . This suggests that these scales all depend heavily on the dipolar properties of solvent molecules and could be used to assess electrostatic forces in a solution or to find a better solvent for separating ion pairs in solution. Another descriptor, c17 (maximum partial charge for a N atom) is the most significant for four scales:  $DN$ ,  $B-2$ ,  $D_S$ , and  $\Delta H^0BF_3$ . This suggests that those scales specifically measure interactions involving hydrogen bond acceptor properties of solvents and can be used for choosing appropriate electron pair donor solvents.

In Table 6, all the scales are listed once more together with the descriptors involved in the QSPR equations. For each of the scales the main physico-chemical phenomena suggested by the descriptors are listed together with the comparison to the ideas of the authors. Most of the scales show good agreement with the original ideas of the authors; in some cases the descriptors even give insight into the mechanisms of the measurement of the scales or describe the set of compounds used for the buildup of the scale. The amount of scales treated and the generally good agreement achieved make it both impossible and unnecessary to discuss each scale here in detail, nor was it our aim, but some interesting results may be pointed out.

The probe for the  $P_S$  scale is a perfluoro compound, and thus the scale has a tendency for F-atom-specific distortions, accounted for the descriptor p04 (psa of F atoms). In case of the  $D_\pi$  and  $E_{CT(\pi)}$  scales the size and shape descriptors point out that the scales are built to account for  $\pi$  interactions of solvents with soft acceptors.

**Table 6.** QSPR Models Compared to the Methodology from Table 1<sup>a</sup>

	scale	R <sup>2</sup>	D1	D2	D3	D4	descriptors indicate influence of	result of comparison
1	ET	0.880 <sup>d</sup>	c16	c10	h14	c09	dipolarity, acidity	agree well
2	DN	0.837	c17	c27	p05	e18	polar, polarizability, charge onN	agree
3	SA	0.926	h03	e11	e04		H-bd, reactivity	agree well
4	P <sub>S</sub>	0.832	e17	c06	p04	p03	dipolar, specific for subst (F)	agree well
5	B	0.903	c15	b04	g05	e03	base	agree
6	E	0.953	h15	t08	e08		polarity, polarizability, acidity	agree well
7	Y <sup>2</sup>	0.949	e17	h13	c03	e15	polarity, H-ba	agree
8	P	0.955	c05	e01	t09	c15	polarizability, charge distribution	agree well
9	SB <sup>-2</sup>	0.992	b06	b05	c22	e03	basicity, some specific infl.	agree
10	B-2	0.933	c17	c18	e06	b09	N, O,-Lewis bases	agree
11	α	0.919	b13	blO	h16	tlO	acidity, OH, NH, shape	agree well
12	β	0.901	e18	b12	c19	h01	polarizability, e1 pair donor	agree
13	log(d)	0.910	e17	h12	tlO	e07	dipolarity, H-b, shape	agree
14	J <sup>2</sup>	0.922	e17	h1O	c13	e05	dipolarity, ch. distribution, H-b	agree
15	M	0.913	c26	e01	c24	g09	polarizability, ch. distribution	agree well
16	N	0.915	e17	hl 1	c29	c02	dipolarity, charge distr., H-b,	agree well
17	P <sub>y</sub>	0.875	p07	o01	c11	h06	charge distr., dipolarity	agree well
18	AN	0.956	b08	c16	h02	t05	strong H-b, shape,	agree
19	A	0.957	b08	t04	blO	cO1	acidic, H-bd	agree well
20	BB <sup>3</sup>	0.755	c23	c17	b01	p06	basicity, N, C, O	agree well
21	ΔH <sup>0</sup> BF <sub>3</sub>	0.930	c17	c25	g07	h18	H-ba, basicity	agree well
22	E <sub>B</sub>	0.978	b16	t04	h04		H-bd, acidic	agree
23	Z	0.920	b16	o01	h19	h17	dipolarity, H-b, H-ba	somewhat agree
24	D <sub>S</sub>	0.884	c17	e13	b03	c21	atom specific, softer	agree well
25	Δν <sub>OH</sub>	0.867	c20	c07	b03	e18	basic, covalent interaction	agree well
26	π <sup>*</sup>	0.900	c12	e03	e17	g04	dipolarity, non specific	agree well
27	E <sub>BB</sub>	0.816	e17	c28	c01	g02	dipolarity, polarizability	agree well
28	CB <sup>-2</sup>	0.999	g06	c29	tl1		shape/size, charge	agree well
29	Δν <sub>Cl</sub>	0.906	c20	p02	e09		H-b, covalent,	agree
30	S	0.964	c30	c32	h08		charge distribution	agree
31	E <sup>*</sup> <sub>MLCT</sub> <sup>3</sup>	0.960	o01	c08	b07		charge distribution, dipolarity	agree well
32	D <sub>π</sub> <sup>3</sup>	0.941	g07	e19	t06		size, shape, electron distribution	agree
33	(SPP <sup>N</sup> ) <sup>3</sup>	0.906	e17	g08	c33		dipolarity, charge distr., polarizab.	agree
34	δ	0.924	h05	o01	g09		dipolarity, H-bd, polarizability	agree
35	μ	0.927	p08	p01	p07		psa of S(soft) C(medium) O(hard)	agree well
36	χ <sub>R</sub>	0.889	h19	c31	glO		charge distrib., polarizability	agree
37	E <sub>T</sub> <sup>SO</sup>	0.965	b15	t04	h13		H-b, shape	agree
38	X	0.963	h11	e02	b11		H-b, interactions	agree 39
39	E <sub>CT(π)</sub>	0.845	c34	h09	g01	t07	shape/size, charge	agree 40
40	S'	0.936	c10	h14	t02		charge distribution	agree
41	π <sup>*</sup> <sub>aso</sub>	0.934	e10	e17	c03		H-b, dipolar	agree
42	E <sub>CT(A)</sub>	0.923	h05	t01	b02		H-b, dipolar, shape	agree
43	D <sub>H</sub>	0.837	c14	c15	b14		atom specific	agree well
44	XX	0.890	e16	t03	e14		electron distribution	agree well
45	Φ	0.958	c04	e03			charge distribution	agree well

<sup>a</sup> H-b stands for hydrogen bonding, H-ba and H-bd are hydrogen bond acceptor and donor, respectively, and psa stands for partial surface area.

In some cases the findings from the equation do not match very well with the original idea of the scale. In the case of the Z scale, the descriptor for hydrogen bonding acceptor properties does not fit well into the original idea.

It is also seen that the descriptors used in the case of hydrogen bond donor and acidity scales are of more general type, while the basicity and hydrogen bond acceptor scales are often described using descriptors for the key atoms of the corresponding centers (N, O, S). This shows that while our set has several general descriptors available for acidity, there are no similarly good general descriptors for basicity.

## CONCLUSIONS

We have demonstrated that the CODESSA program and its associated set of descriptors can be applied to a wide range of solvent scales to obtain highly significant correlations described quantitatively by equations with just three or four solely theoretical molecular descriptors. The study enables classification of the scales, which provides considerable insight into the physical background of the various scales.

Our work represents, for the first time, that QSPR models for a large number of solvent scales have been developed using only theoretical molecular descriptors. Moreover, these results allow a unified PCA treatment of solvent scales as described in the following paper in this issue.

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**Supporting Information Available:** Table 3 gives the experimental values of the 45 scales for the 65 solvents used in this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## REFERENCES AND NOTES

- (1) (a) Koppel, I.; Palm, V. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum: London, 1972; pp 203–280. (b) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: New York, 1988. (c) Politzer, P.; Murray,



- J. S. *Quantitative Treatments of Solute-Solvent Interactions*; Elsevier: New York, 1994. (d) Fowler, F. W.; Katritzky, A. R.; Rutherford, R. J. D. The Correlation of Solvent Effects on Physical and Chemical Properties. *J. Chem. Soc. B* **1971**, 460–489. (e) Soukup, R. W.; Schmid, R. Metal Complexes as Color Indicators for Solvent Parameters. *J. Chem. Educ.* **1985**, 62, 459–462. (f) Sandström, M.; Persson, I.; Persson, P. A Study of Solvent Electron-Pair Donor Ability and Lewis Basicity Scales. *Acta Chem. Scand.* **1990**, 44, 653–674. (g) Marcus, Y. The Properties of Organic Liquids that are Relevant to their Use as Solvating Solvents. *Chem. Soc. Rev.* **1993**, 409–416. (h) Joerg, S.; Drago, R. S.; Adams, J. Donor-acceptor and Polarity Parameters for Hydrogen Bonding Solvents. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2431–2438. (i) Paéz, J. A.; Campillo, N.; Elguero, J. Empirical Modelling of Solvent Polarity Scales. *Gazz. Chim. Ital.* **1996**, 126, 307–311.
- (2) Drago, R. S. A Unified Scale for Understanding and Predicting Non-Specific Solvent Polarity: A Dynamic Cavity Model. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1827–1838.
  - (3) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. AM1: A New General Purpose Quantum Mechanical Molecular Model. *J. Am. Chem. Soc.* **1985**, 107, 3902–3909.
  - (4) Stewart, J. J. P. *MOPAC Manual* 6.0; QCPE No 455, Seiler F. J. Research Laboratory, 1990.
  - (5) Katritzky, A. R.; Lobanov, V. S.; Karelson, M. *CODESSA Reference Manual Version 2.0*; Gainesville, 1994.
  - (6) Katritzky, A. R.; Lobanov, V. S.; Karelson, M. QSPR: The Correlation and Quantitative Prediction of Chemical and Physical Properties from Structure. *Chem. Soc. Rev.* **1995**, 279–287.
  - (7) Katritzky, A. R.; Maran, U.; Karelson, M.; Lobanov, V. S. Prediction of Melting points for the Substituted Benzenes: A QSPR Approach. *J. Chem. Inf. Comput. Sci.* **1997**, 37, 913–919.
  - (8) Katritzky, A. R.; Ignatchenko, E. S.; Barcock, R. A.; Lobanov, V. S.; Karelson, M. Prediction of Gas Chromatographic Retention Times and Response Factors Using a General Quantitative Structure-Property Relationship Treatment. *Anal. Chem.* **1994**, 66, 1799–1807.
  - (9) (a) Huibers, P. D. T.; Lobanov, V. S.; Katritzky, A. R.; Shah, D. O.; Karelson, M. Prediction of Critical Micelle Concentration Using a Quantitative Structure-Property Relationship Approach. 1. Nonionic Surfactants. *Langmuir* **1996**, 12, 1462–1470. (b) Huibers, P. D. T.; Lobanov, V. S.; Katritzky, A. R.; Shah, D. O.; Karelson, M. Prediction of Critical Micelle Concentration Using a Quantitative Structure-Property Relationship Approach. 2. Anionic Surfactants. *J. Colloid Interface Sci.* **1997**, 187, 113–120.
  - (10) Katritzky, A. R.; Mu, L.; Karelson, M. A QSPR Study of the Solubility of Gases and Vapors in Water. *J. Chem. Inf. Comput. Sci.* **1996**, 36, 1162–1168.
  - (11) Katritzky, A. R.; Rachwal, P.; Law, K. W.; Karelson, M.; Lobanov, V. S. Prediction of Polymer Glass Transition Temperatures Using a General Quantitative Structure-Property Relationship Treatment. *J. Chem. Inf. Comput. Sci.* **1996**, 36, 879–884.
  - (12) (a) Kier, L. B.; Hall, L. H. *Molecular Connectivity in Structure-Activity Analysis*; Wiley: New York, 1986. (b) Karelson, M.; Lobanov, V. S.; Katritzky, A. R. Quantum-Chemical Descriptors in QSAR/QSPR Studies. *Chem. Rev.* **1996**, 96, 1027–1043. (c) Stankevich, M. I.; Stankevich, I. V.; Zefirov, N. S. Topological Indices in Organic Chemistry. *Russ. Chem. Rev. (Engl. Transl.)* **1988**, 57, 191–208.
  - (13) Katritzky, A. R.; Tamm, T.; Wang, Y.; Karelson, M. A Unified Treatment of Solvent Properties. *J. Chem. Inf. Comput. Sci.* **1999**, 39, 692–698.
  - (14) Reichardt, C. Solvatochromic Dyes as Solvent Polarity Indicators. *Chem. Rev.* **1994**, 94, 2319–2358.
  - (15) Catalán, J.; Díaz, C. A Generalized Solvent Acidity Scale: The Solvachromism of o-tert-Butylstilbazolium Betaine Dye and its Homomorph o,o'-Di-Tert-Butylstilbazolium Betaine Dye. *Liebigs Ann./Recueil* **1997**, 1941–1949.
  - (16) Freed, B. K.; Biesecker, J.; Middleton, W. J. Spectral Polarity Index: A New Method for Determining the Relative Polarity of Solvents. *J. Fluorine Chem.* **1990**, 48, 63–75.
  - (17) Sergeant, M.; Luu, R. P. T.; Elguero, J. Statistical Analysis of Solvent Scales. Part 1. *Anales de Química Int. Ed.* **1997**, 93, 71–75.
  - (18) Koppel, I. A.; Paju, A. I. Parameters of General Basicity of Solvents. *Org. React.* **1974**, 39, 121–136.
  - (19) Catalán, J.; Díaz, C.; López, V.; Pérez, P.; de Paz, J.-L. G.; Rodríguez, J. G. A Generalized Solvent Basicity Scale: The Solvatochromism of 5-Nitroindoline and its Homomorph 1-Methyl-5-Nitroindoline. *Liebigs Ann.* **1996**, 1785–1794.
  - (20) Taft, R. W.; Kamlet, M. J. The Solvatochromic Comparison Method. 2. The  $\alpha$ -Scale of Solvent Hydrogen-Bond Donor (HBD) Acidities. *J. Am. Chem. Soc.* **1976**, 98, 2886–2894.
  - (21) Kamlet, M. J.; Taft, R. W. The Solvatochromic Comparison Method. I. The  $\beta$ -Scale of Solvent Hydrogen-Bond Acceptor (HBA) Basicities. *J. Am. Chem. Soc.* **1976**, 98, 377–383.
  - (22) Dong, D. C.; Winnik, M. A. The Py Scale of Solvent Polarities. Solvent Effects on the Vibronic Fine Structure of Pyrene Fluorescence and Empirical Correlations with  $E_r$  and  $Y$  Values. *Photochem. Photobiol.* **1982**, 35, 17–21.
  - (23) Mayer, U.; Gutmann, V.; Gerger, W. The Acceptor Number – A Quantitative Empirical Parameter for the Electrophilic Properties of Solvents. *Monatsh. Chem.* **1975**, 106, 1235–1257.
  - (24) Janowski, A.; Turowska-Tyrk, I.; Wrona, P. K. Use of Stable 2,2,6,6-Tetramethylpiperidine N-Oxyl Radical for the Measurements of Lewis Acidity of Solvents. *J. Chem. Soc., Perkin Trans. 2* **1985**, 821–825.
  - (25) Persson, I.; Sandström, M.; Goggin, P. L. On the Coordinating Properties of some Solvents. A Vibrational Spectroscopic Study of Mercury(II) Halides and Antimony(V) Chloride in Solution; New Concepts for Lewis Basicity Scales of Solvents. *Inorg. Chim. Acta* **1987**, 129, 183–197.
  - (26) Kosower, E. M. The Effect of Solvent on Spectra. I. A New Empirical Measure of Solvent Polarity: Z-Values. *J. Am. Chem. Soc.* **1958**, 80, 3253–3260.
  - (27) Laurence, C.; Queignec-Cabanetos, M.; Dziembowska, T.; Queignec, R.; Wojtkowiak, B. 1-Iodoacetylenes. 1. Spectroscopic Evidence of Their Complexes with Lewis Bases. A Spectroscopic Scale of Soft Basicity. *J. Am. Chem. Soc.* **1981**, 103, 2567–2573.
  - (28) Kamlet, M. J.; Abboud, J. L. M.; R. Taft, W. The Solvatochromic Comparison Method. 6. The  $\pi^*$  Scale of Solvent Polarities. *J. Am. Chem. Soc.* **1977**, 99, 6027–6038.
  - (29) Manuta, D. M.; Lees, A. J. Solvent and Substituent Effects on the Lowest Energy Excited States of  $M(CO)_4$ (diimine) ( $M = Cr, Mo, W$ ) Complexes. *Inorg. Chem.* **1983**, 22, 3825–3828.
  - (30) Brooker, L. G. S.; Craig, A. C.; Heseltine, D. W.; Jenkins, P. W.; Lincoln, L. L. Color and Constitution. XIII. Merocyanines as Solvent Property Indicators. *J. Am. Chem. Soc.* **1965**, 87, 2443–2450.
  - (31) Walter, W.; Bauer, O. H. Zur Solvatochromie von *N,N*-(Dimethyl)-thiobenzamid-*S*-Oxid. (The Solvatochromism of *N,N*-Dimethylthiobenzamide *S*-Oxide.) *Liebigs Ann. Chem.* **1977**, 421–429.
  - (32) Kaim, W.; Olbrich-Deussner, B.; Roth, T. Specific Solvatochromism of the Prototypical Olefin Complexes  $(\eta^2\text{-TCNE})M(CO)_5$  ( $M = Cr, W$ ) Resulting from  $n$  and  $\pi$  Donation of Aprotic Solvents toward the  $\pi$ -Acceptor Ligand. *Organometallics* **1991**, 10, 410–415.
  - (33) Buncel, E.; Rajagopal, S. Solvatochromic Studies of Novel Azo Merocyanine Dyes. The  $\pi^*_{azo}$  Scale of Solvent Polarity. *J. Org. Chem.* **1989**, 54, 798–809.
  - (34) Davis, K. M. C. Charge-Transfer Complexes. Part III. Solvent Shifts of the Charge-transfer Band of Complexes formed between Halide Ions and Organic Electron Acceptors. *J. Chem. Soc. B* **1967**, 1128–1130.
  - (35) David, J. G.; Hallam, H. E. Infra-red Solvent Shifts and Molecular Interactions-X Triatomic Molecules,  $CS_2$ ,  $COS$  and  $SO_2$ . *Spectrochim. Acta* **1967**, 23A, 593–603.
  - (36) Dubois, J. E.; Bienvenüe, A. Caractere Ambivalent Des Effects De Solvation Sur Certaines Transitions Electroniques. (The Ambivalent Nature of Solvation Effects on Certain Electronic Transitions.) *Tetrahedron Lett.* **1966**, 1809–1819.
  - (37) Gutmann, V.; Wychera, E. Coordination Reactions in Non Aqueous Solutions – The Role of the Donor Strength. *Inorg. Nucl. Chem. Lett.* **1966**, 2, 257–260.
  - (38) Maria, P.-C.; Gal, J.-F. A Lewis Basicity Scale for Nonprotogenic Solvents: Enthalpies of Complex Formation with Boron Trifluoride in Dichloromethane. *J. Phys. Chem.* **1985**, 89, 1296–1304.
  - (39) Drago, R. S.; Dadmun, A. P.; Vogel, G. C. Addition of New Donor to the E and C Model. *Inorg. Chem.* **1993**, 32, 2473–2479.
  - (40) Oshima, T.; Arikata, S.; Nagai, T. Solvent Effects in the Reaction of Diazodiphenylmethane with Tetracycanoethylene: a New Empirical Parameter of Solvent Basicity. *J. Chem. Res. S* **1981**, 204–205.
  - (41) Marcus, Y. Linear Solvation Energy Relationship. A Scale Describing the “Softness” of Solvents. *J. Phys. Chem.* **1987**, 91, 4422–4428.
  - (42) Fletcher, K. A.; McHale, M. E. R.; Coym, K. S.; Acree, W. E., Jr. Solubility of Trans-stilbene in Organic Nonelectrolyte Solvents. Comparison of Observed versus Predicated Values Based upon Mobile Order Theory. *Can. J. Chem.* **1997**, 75, 258–261.
  - (43) Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S. Solvent Effect on Chemical Reactivity. Evaluation of Anion and Cation Solvation Components. *J. Am. Chem. Soc.* **1983**, 105, 502–513.
  - (44) Brownstein, S. The Effect of Solvents upon Equilibria, Spectra, and Reaction Rates. *Can. J. Chem.* **1960**, 38, 1590–1596.
  - (45) (a) Mu, L.; Drago, R. S.; Richardson, D. E. A Model based QSPR Analysis of the Unified Non-specific Solvent Polarity Scale. *J. Chem. Soc., Perkin Trans. 2* **1998**, 159–167. (b) Katritzky, A. R.; Mu, L.; Karelson, M. QSPR Treatment of the Unified Nonspecific Solvent Polarity Scale. *J. Chem. Inf. Comput. Sci.* **1997**, 37, 756–761.