Electrostatic Potentials of Molecules and Prediction of the Lewis Acid-Base Properties of Solvents, Part II. Application of Electrostatic Parameters

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Summary. Electrostatic parameters, *UN* and *UP*, introduced previously, have been applied to predict solvent acid and base properties. The *UN* parameter correlates well with the electrostatic component of solvent basicity. This parameter also significantly improves correlations between Koppel-Paju, Kamlet-Taft and Gutmann basicity scales. The *UP* parameter combined with Mullikan charges at hydrogen atoms of the solvent molecules allows an estimation of solvent acidity parameters in the frame of the two-parameter similarity model. The results show that parameters computed with the MNDO method for isolated molecules are suitable for molecules of nonaqueous solvents in liquid state.

Keywords. Basicity; Acidity; Electrostatic potential; Solvent effect.

Elektrostatische Potentiale von Molekülen und Voraussage von Lewis-Säure-Base-Eigenschaften von Lösungsmitteln, 2. Mitt.: Anwendung elektrostatischer Parameter

Zusammenfassung. Die in der vorhergehenden Arbeit eingeführten elektrostatischen Parameter *UN* und *UP* wurden zu Vorhersagen von Säure- und Base-Eigenschaften von Lösungsmitteln angewandt. Der *UN*-Parameter korreliert gut mit der elektrostatischen Komponente der Lösungsmittelbasizität und verbessert auch signifikant Korrelationen zwischen der Koppel-Paju, Kamelt-Taft und Gutmann'schen Basizitätsskala. Der *UP*-Parameter, in Kombination mit Mullikan-Ladungen an den Wasserstoffatomen der Lösungsmittelmoleküle, erlaubt die Abschätzung von Solvens-Aciditäts-Parametern im Rahmen eines Zweiparameter-Vergleichsmodells. Die Ergebnisse zeigen, daß die über die MNDO-Methode für isolierte Moleküle berechneten Parameter zur Beschreibung von nichtwäßrigen Lösungsmitteln geeignet sind.

Introduction

Much of chemical and biochemical processes proceed in liquid solutions and involve ionic species. In all these systems the ions interact with one another; the extent of the interactions and the rate of any reactions in which the ions take part depend strongly on the nature of the ion-solvent interactions.

Solvents can be characterized in many ways [1 − 6]. Sometimes the division into polar and nonpolar solvents is useful. The former category is additionally

subdivided into protic and aprotic ones; both classes play a dominant role in ion solvation. The commonly quoted measures of solvent polarity, e. g. dipole moment and dielectric constant, are not sufficient to describe quantitatively this phenomenon, and the electron pair donation and acceptance abilities of the solvents are of great importance. The hydrogen bond acceptance and donation abilities are also important in this respect.

The previous work [7] has considered the electrostatic potentials in the vicinity of isolated solvent molecules of typical nonaqueous solvents. Consequently, two computable parameters, $UN(R)$ and $UP(R)$, were introduced to describe the Coulombic interactions of a solvent with a cation and an anion of radius R. Abbreviations UN and UP were proposed to denote $UN(R)$ and $UP(R)$ calculated for a reference ionic radius of $R = 133$ pm, and corresponding values were tabulated for a number of solvents. This paper shows that UN and UP can be used to predict the solvation power of solvents. It is also shown that the UN values can be useful to interpret experimental parameters characterizing the propensity of a solvent to accept a hydrogen bond or to donate an electron pair.

Results and Discussion

Gas Phase Binding of Ions and Electrostatic Potential of Molecules

In the beginning it was of interest to learn how the computed UN and UP values represent the true ion-solvent interaction energies. Of the properties examined, the gas-phase enthalpies of the formation of the 1 : 1 solvent-potassium(I) adducts seem to be of largest significance. Fortunately, a list of corresponding ΔH_f values has been published [8] and some of these were used by us; comparison of them to the reference ($R = 133$ pm) UN values is presented in Fig. 1.
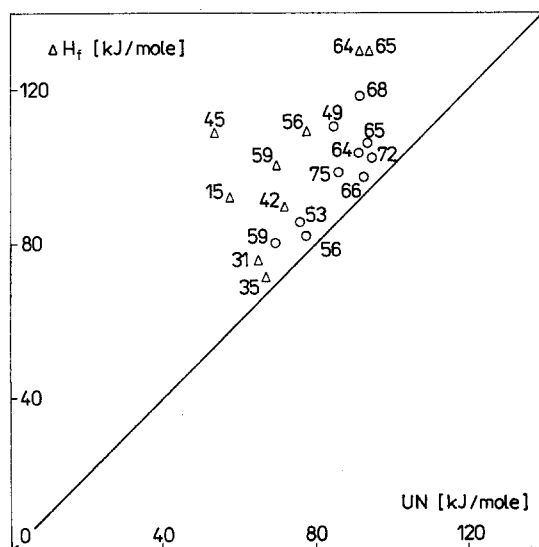

Fig. 1. Experimental enthalpy of binding of K^+ ions to isolated solvent molecules *versus* calculated [7] electrostatic energy. $\triangle$-Ref. [8], $\odot$ R. W. Taft, private communication. Solvent numbers according to Table 1 in Ref. [7]

The interdependence from this figure needs some comments. First, the data set is necessarily incomplete and pertains to 15 solvents only. Second, the full-drawn line in Fig. 1 relates to the situation in which pure Coulombic interactions occur between both components of the adducts. In this situation we assume that the discrepancies of the experimental ΔH_f values with this line may be due to the polarization of the solvent molecule as well as the charge transfer from the solvent to the ion. Nevertheless, one important trend should be emphasized: the negative ΔH_f values increase visibly with an increasing of UN, as it can be expected. This finding is encouraging since we meet no case with a computed electrostatic energy larger than the observed total energy of bonding; therefore no "scaling" or "correcting" is necessary. Here, we will not analyze data for other cations but it is worth to notice as an example that recently published data [9] on the formation of solvent-Li^+ adducts in the gas-phase depend upon the UN parameter in a manner very similar to that of potassium ions. Thus, we may expect that our UN values reflect satisfactorily the real electrostatic potentials near electron-donating atoms of the solvent molecules. It should be added, however, that experimental data for ΔH_f from different measurements are significantly divergent [8, 10] and, therefore, more rigorous discussion of the problem is rather impossible.

Next, we have considered the interaction of a single monoatomic anion and a single bipolar solvent molecule in the gas phase. The fluoride ion was chosen because its crystal ionic radius is very similar to those for the potassium cation. In this case, the ΔH_f values are available only for acetonitrile and few protic solvent molecules [11]. Moreover, an analysis analogous to that described above shows that the proper electrostatic factor UP [7] represents only ⅔ of the overall interaction energy for water, ½ for CH_3CN and even less for alcohols. However, this situation can be rationalized. Anions generally accept hydrogen bonds from protic solvents, and this ability is particularly large for the fluoride ion [5]. Thus, correct description of the electrostatic contribution to the ion-solvent interactions should help much more in the analysis of solvent basicity than of solvent acidity.

Electrostatic Contribution to Solvent Basicity

It is well known that the quantities related to the electron pair donation abilities of solvents are of great importance for ion solvation [4 − 6]. These include, explicitly or implicitly, also measures of the Lewis basicity of solvents and, where relevant, their abilities to donate and accept a hydrogen atom towards the formation of a hydrogen bond. Many of them, often called basicity parameters, have been proposed in the literature (for reviews see e. g. [5, 6, 12] and references therein). Although these parameters were obtained with very different standard processes and procedures, there exist satisfactory linear relationships between most of them, particularly when solvents with highly specific interaction capabilities (e. g. protic solvents) are correlated separately [13, 14]. Hence only three, B, β and DN will be discussed here.

The empirical B-scale of Koppel and Paju [15] is defined on the basis of the IR spectrum of phenol-solvent adduct in dilute CCl_4 solution. This implies, of course, that the hydrogen bond acceptance ability of the solvent is the dominant factor contributing to the B value. It is also clear that the latter parameter should be treated as a selected member of a family of similar, strongly correlated parameters based on other hydrogen-bond donors [6, 15].

Table 1. Basicity and acidity parameters of selected solvents[a]

No.	Solvent	B	β	DN	$10^3 q_H$[b]	E_T	AN
1	Tetramethylsilane	0	(−0.08)	(−3.2)	2.2	30.7	(4.5)
2	Cyclohexane	0	0.00	(−3.5)	5.0	30.9	0.0
3	Carbon tetrachloride	0	0.00	0.0[k]	0.0	32.4	8.6
4	Chloroform	14	0.00	(−0.5)	87.8	39.1	23.1
5	Methylene chloride	23	(0.07)	(1.7)	55.6	40.7	20.4
6	o-Dichlorobenzene	28	(0.05)	(1.5)	94.5	38.0	(15.7)
7	Chlorobenzene	38	0.07	(3.2)	77.9	36.8	(11.2)
8	Benzene	48	0.10	0.1[k]	59.3	34.3	8.2
9	tert-Butyl chloride	64	(0.20)	(6.5)	12.8	−	(9.6)
10	Nitrobenzene	65	0.39	8.1	85.7	41.2	14.8
11	Ethyl trichloroacetate	87	0.85	(9.4)	34.7	−	(13.8)
12	Furan	103	(0.18)	(7.0)	117.5	36.0	(15.0)
13	Chloroacetonitrile	117	(0.29)	(10.4)	52.6	−	(18.9)
14	Biacetyl	121	0.31	(10.6)	26.5	−	(11.7)
15	Ethyl monochloroacetate	125	0.35	12.8[m]	57.8	39.4	(16.5)
16	Ethyl formate	126[e]	0.36	17.0	99.9	40.9	(16.7)
17	Dimethyl carbonate	136	0.38	15.2	27.5	41.1	(9.9)
18	Ethyl benzoate	142	0.41	(15.9)	78.3	38.1	(11.7)
19	Vinyl acetate	143	(0.40)	(14.5)	85.1	38.0	(14.2)
20	DMCFA[c]	144	(0.42)	(14.9)	8.0	−	(15.1)
21	Diethyl carbonate	145	0.40	16.0	12.0	37.0	(8.1)
22	Benzyl cyanide	155	(0.40)	15.1	65.1	42.7	14.9
23	Benzonitrile	155	0.41	13.0	69.3	41.5	15.5
24	Anisole	155	0.22	(13.4)	71.1	37.1	(10.3)
25	Acetonitrile	160	0.31	14.6	20.8	45.6	18.9
26	Nitromethane	160	0.39[l]	2.7[n]	49.0	46.3	20.5
27	Propionitrile	162	0.37	16.1	31.6	43.7	(12.0)
28	Methyl acetate	170	0.42	16.4	27.3	40.0	10.7
29	2,6-Difluoropyridine	170	(0.45)	(16.5)	97.0	43.3	(21.0)
30	Benzaldehyde	180	0.42[l]	(17.0)	75.1	−	(12.9)
31	Ethyl acetate	181	0.45	17.1	27.1	38.1	9.3
32	Epichlorhydrine	183	(0.38)	(14.6)	58.6	44.5	(16.4)
33	DMTFA[d]	185	0.46	(16.3)	15.6	−	(17.2)
34	Ethylene carbonate	196	(0.53)	16.4	40.8	48.6	(21.6)
35	Acetophenone	202	0.49	(18.4)	77.0	40.6	(12.4)
36	Butanone-2	209	0.48	17.4	24.2	41.3	(12.0)
37	γ-Butyrolactone	216[f]	0.49	(20.5)	48.7	44.3	(16.0)
38	Acetone	224	0.48	17.0	22.0	42.2	12.5
39	N,N-Dimethylcyanamide	226	(0.54)	(20.3)	5.9	43.8	(13.4)
40	1,4-Dioxane	237	0.37	14.8	11.5	36.0	10.8
41	Cyclopentanone	239[f]	0.52	(19.5)	36.1	39.4	(9.7)
42	Cyclohexanone	242	0.53	17.8	33.4	39.8	(10.9)
43	Formamide	270	0.66	(23.8)	189.4	56.6	39.8
44	Di-n-propyl ether	279	0.46	17.8	23.3	34.0	(9.1)
45	Diethyl ether	280	0.47	19.2	5.7	34.5	3.9
46	Tetrahydrofuran	287	0.55	20.5	20.9	37.4	8.0
47	N-Methylformamide	287	(0.63)	(24.3)	188.8	54.1	32.1
48	Tetrahydropyran	290	0.53	(20.0)	20.5	36.6	(7.2)

Table 1 (continued)

No.	Solvent	B	β	DN	$10^3 q_H$[b]	E_T	AN
49	N,N-Dimethylformamide	291	0.69	26.6	55.8	43.8	16.0
50	N,N,N',N'-Tetramethylurea	340[g]	0.80	29.6	6.6	41.0	(8.9)
51	N,N-Dimethylacetamide	343	0.76	27.8	30.7	43.7	13.6
52	N,N'-Dimethylpropyleneurea	356	(0.74)	(29.3)	15.1	42.1	(12.2)
53	1-Methyl-2-pyrrolidinone	357[h]	0.78	27.3	39.6	42.2	13.3
54	N,N-Dimethylaniline	372[i]	0.33	(20.2)	70.0	36.5	(9.2)
55	3,5-Dichloropyridine	374	0.42	(22.0)	106.4	−	(17.6)
56	Pyridine-N-oxide	441[j]	0.85	(33.8)	115.4	−	(19.6)
57	Pyridine	472	0.64	34.0	83.4	40.5	14.2
58	Ammonia	473	(0.66)	(29.4)	76.0	−	(20.5)
59	4-Methylpyridine	495	0.67	(31.5)	83.7	−	(11.8)
60	2,4,6-Trimethylpyridine	531	0.78	(32.7)	68.2	36.4	(10.3)
61	2,6-Dimethylpyridine	535	0.76	(33.0)	70.3	36.6	(10.7)
62	Cyclopropylamine	548[l]	0.60	(32.3)	125.3	−	(23.5)
63	Diethylamine	637	(0.77)	(36.2)	115.3	35.4	9.4
64	Triethylamine	650	0.71	31.7	−0.5	32.1	1.4

[a] If not stated otherwise, values of parameters B, β, DN, E_T, and AN are from Refs. [15], [17], [19], [6], and [35]; values of β, DN, and AN given in parentheses were estimated from Eqs. (4), (5), and (6);

[b] Calculated (this work), see text;

[c] N,N-Dimethylchloroformate, Cl-CO-$N(CH_3)_2$;

[d] N,N-Dimethyltrifluoroacetamide, CF_3-CO-$N(CH_3)_2$;

[e] Calculated (see Ref. [15]) from data for methanol [36];

[f] from Ref. [37];

[g] from Ref. [38];

[h] from Ref. [23];

[i] Calculated from data for p-fluorophenol [39];

[j] from Ref. [40];

[k] from Ref. [4];

[l] Calculated with linear regression with pK_{HB}, Ref. [41];

[m] from Ref.[42];

[n] Excluded from correlation (5), see Ref. [19] for discussion

The β scale of Kamlet and Taft [16, 17] was established by UV/VIS spectroscopic method. To determine the β values [2, 16, 17] the absorption wavenumber shifts of 4-nitroaniline relative to N,N-diethyl-4-nitroaniline were measured in a series of solvents. The basicity scale was established by the deviation of hydrogen-bond-accepting solvents from linear relationships existing for non-hydrogen-bond-accepting media. Consequently, the discussed values measure effectively the ability of a solvent molecule to the hydrogen bond acceptance.

Of particular importance for the determination of the Lewis basicity of a solvent are the donor numbers, DN, introduced by Gutmann [4, 18] and developed by his school. The parameter is defined as the negative enthalpy of the reaction of an electron-pair-donating solvent with antimony(V) chloride as the standard acceptor in a highly diluted 1,2-dichloroethane solution. Thus, the donor number is a mo-

lecular property that reflects the entire interaction of an electron-pair donating solvent with the electron pair acceptor and, therefore it is of particular significance in predicting coordination interactions in solutions. It must be noted that the basic idea of the $-\Delta H_{BF_3}$ solvent parameter introduced more recently by Maria and Gal [19] and DN is quite similar.

Very recently a series of important papers was published on the hydrogen-bond acidity and basicity of molecules. Consequently, new scales of acidity [20] and basicity [12] were constructed using formation constants of hydrogen-bonded complexes [21]. These new scales will be analyzed by us in separate communication; in the current discussion we will limit our scope to more widely accepted parameters.

This short comment should be seen as evidence that the qualification *basicity* is not uniquely defined. Evidently, owing to the different peculiarities of the selected standard processes, corresponding basicity scales are composed of various chemical and/or physical factors, weighted in a different manner in each case under consideration. This leads, however, to the problem of the role of the electrostatic contribution in the overall description of the solvent-solute interactions. Let us analyze, therefore, this problem in more details.

The best starting point for such an investigation are the results of a factor analysis reported in Ref. [14] for various basicity scales. The authors of this interesting paper found that in the case of *aprotic* solvents (the case of hydroxylic ones seems to be complicated [14, 19, 22] and will not be discussed further in this section) basicity parameters can be expressed by the following formula

$$BAS = aF_1 + bF_2 + c \qquad (1)$$

where BAS denotes any basicity scale, F_1 and F_2 stand for the factors mutually orthogonal by definition, whereas a, b and c are regression coefficients. It is noteworthy that in the original report [14] the analysis was performed for 22 solvents, therefore, the procedure of finding F values for each succeeding solvent demands repeating the whole factor analysis again which may alter previously accepted F-parameters. Of course, this is a consequence of the mentioned orthogonality of F_1 and F_2.

Fortunately, there exists another way to exploit relation (1). Let us state that i) the F_2 factor is essentially of electrostatic nature as it was indicated by the correlation of F_2 with corresponding gas-phase ΔH_f values [14] and ii) the latter correlate very well with our UN parameter (c. f. Fig. 1 and discussion presented in previous section). In this situation the dependence between F_2 and UN should also be anticipated. In reality, treating the problem with the least squares procedure (solvents number 3, 9, 11, 12, 15, 30, 33, 37, 38, 42, 43, 49, 56, 57, 59, 64, 65, 67, and 88 from Table 1 in Ref. [7] were used) we have obtained an expression of the following form:

$$F_2 = 0.00828 \, UN - 0.63 \qquad (2)$$

with a correlation coefficient of $r = 0.965$ and a standard deviation $s_{F2} = 0.03$ for the set of 19 solvents (for comments on the selection of reference ion radius see Appendix). The percentage of explanation of variance for variation of F_2 is 93%. Taking into account possible errors in the determination of F_2 parameters as well as in the calculation of UN values, this result can be understood to be satisfactory. The dependence of F_2 on UN according to Eq. (2) is graphically presented in Fig. 2.
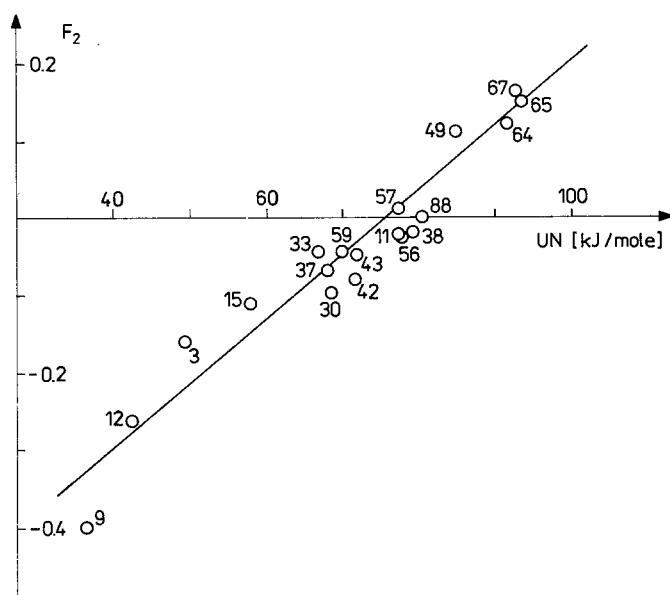
Fig. 2. Dependence between the reference *UN* values (data and solvent numbers from Table 1 in Ref. [7]) and the F_2 factor of solvent basicity (Ref. [14])

This finding seems to be important; it confirms that the F_2 parameter describes really the electrostatic contribution to the basicity of a given molecule. Consequently we suggest that with the knowledge of one basicity scale (e. g. BAS_0) other basicity parameters (BAS_i) can be predicted with the help of an expression of the following form

$$BAS_i = a_i BAS_0 + b_i F_2 + c_i \tag{3}$$

A brief illustration of this hypothesis is presented below. As a primary scale (BAS_0 in Eq. 3), the *B*-values of Koppel and Paju have been chosen because they are known for a large number of solvents [15, 23] and they are also well tested. Some of these values are compiled in Table 1 together with other solvent parameters used in our analysis. Taking into account these data and corresponding *UN* values (solvents number $2-4$, 7, 8, 10, 11, $14-18$, 21, $23-28$, 30, 31, 33, $35-38$, $40-46$, $48-51$, $53-57$, $59-62$, and 64 from Table 1 were used) we have found the two-parameter regression

$$\beta = 0.000907\,B + 0.00492\,UN - 0.090 \tag{4}$$

with $r = 0.964$ and $s_\beta = 0.06$ for all 47 solvents with available experimental data. Linear correlation of β versus B reveals a correlation coefficient 0.821, while the two-parameter treatment of β as a function of B and calculated dipole moment [7] gives $r = 0.907$ for the same set of solvents. Thus, the validity of regression (4) is evident; this conclusion may also be drawn on the basis of the Fisher-Snedecor *F*-test. Similarly, the regression (solvents number 3, 8, 10, $15-17$, $21-23$, 25, 27, 28, 31, 34, 36, 38, 40, 42, $44-46$, $49-51$, 53, 57, and 64 were used)

$$DN = 0.0491\,B + 0.1480\,UN - 3.52 \tag{5}$$

with $r = 0.970$ and $s_{DN} = 1.9$ ($N = 27$) is significantly better than the linear correlation of DN versus B ($r = 0.891$) and the planar regression including B and dipole moments ($r = 0.917$). Exemplary applications of Eqs. (4) and (5) are also shown in Table 1 which contains predicted values of β and DN for many solvents. Moreover, we hope that both regressions will be useful also in future, especially in the cases when direct measurements of these basicity parameters are difficult or even impossible.

It should be mentioned here that in the literature only few attempts occur to predict solvent basicity parameters. Planar regressions that may be applied to predict corresponding β-values from known substituent constants of the Hammett and Taft type have been presented [24] (see also [12]). Unfortunately, each of these regressions are limited to the selected sets of solvents.

Molecular electrostatic potentials calculated in the CNDO/2 approximation have been recently [25] successfully correlated with Brönsted basicity constants of amines in aqueous solution. Nevertheless, this approach leads to separate regression lines for different classes of amines; thus it is not generally applicable.

Also very recently, Lewis [26] presented a linear relation of the β scale to calculated dipole moments divided by the differences of the HOMO and the LUMO energies; the calculations were performed using the MINDO/3 method. However, a correlation coefficient $r = 0.813$ for 14 selected solvents is rather unsatisfactory.

In our opinion it seems to be evident that the UN parameter gives much better prediction of the electrostatic portion of basicity than e. g. dipole moments. However, complete theoretical predictions of observed solvent basicity need a good approximation not only for the electrostatic part of the interaction, but also for the non-electrostatic one (factor F_1 see [14]). Certainly, this will need additional efforts in future.

Approximate Expressions for the Solvent Acidity

Generally, a method for an analysis of solvent basicity may not be directly suited for parameters of solvent acidity; the lack of factor analysis complicates considerably an acceptable discussion. The UP parameter, which was proposed [7] to describe the energy of electrostatic interactions of an anion with radius R with a molecule of solvent, is also inadequate. Analysis of the interaction of the fluoride anion with some solvents indicates clearly (c. f. previous section) that UP explains only a small part of the actual interaction. Therefore, it was necessary to try other models.

Of course, the problems of acidity and basicity may not be treated separately: to measure the strength of an acid we always use a probe base interacting with it. It should be kept in mind that the non-electrostatic component of basicity, F_1 from Eq. (1) is proportional to the enthalpy of protonation of the base [14]. As a consequence proton-like centers of an acidic molecule should contribute to the strength of the acid. Qualitatively, the more similar the hydrogen atom is to a "naked" proton, the stronger is the given acid. On the other hand, from the quantitative point of view, it has been recognized (see e. g. [27]) that it is *the square* of the cation electric charge which is significant in solvation of basic solvents.

Taking into account these ideas we have considered the partial Mullikan charges at the hydrogen atoms of solvent molecules. We propose q_H, the molecular parameter standing for the largest of the Mullikan charge at the hydrogen atom in the molecule; at the same time we expect that a molecule of an acid interacts with a corresponding base by the most charged hydrogen atom, and that the energy of

Table 2. Acidity parameters of selected solvents

No.	Solvent	$10^3 q_H{}^a$	$E_T{}^b$	AN^c
1	Tetramethylguanidine	112.0	39.3	(18.3)
2	3-Pentanone	24.1	41.3	(11.5)
3	Ethylenediamine	106.9	42.0	20.9
4	N,N'-Dimethylethyleneurea	7.9	42.5	(12.2)
5	2-Methyl-2-propanol	178.3	43.3	27.1
6	2-Cyanopyridine	2.1	44.2	(19.1)
7	Methyl formate	102.5	45.0	(17.6)
8	N-Methyl-oxazolidone	29.8	45.0	(16.6)
9	Propylene carbonate	43.1	46.6	18.3
10	2-Pyrrolidinone	202.8	48.3	(36.7)
11	2-Propanol	177.9	48.4	33.5
12	1-Butanol	180.7	50.2	36.8
13	1-Propanol	179.7	50.7	37.3
14	2-Aminoethanol	182.3	51.8	33.7
15	Ethanol	180.0	51.9	37.1
16	Methanol	181.9	55.4	41.3
17	2-Chloroethanol	188.7	55.5	(39.9)
18	2-Cyanoethanol	187.1	59.6	(40.3)
19	2,2,2-Trifluoroethanol	203.5	59.8	53.5
20	Phenol	194.6	61.4	(37.1)
21	Water	162.8	63.1	54.3
22	Hexafluoroisopropanol	219.4	65.3	(63.5)
23	γ-pyron	105.4	–	(18.7)
24	N-Methylimidazole	125.8	–	(24.4)
25	N-Methylsydnone	146.1	–	(37.5)

^{a} Calculated (this work), see text;
^{b} from Ref. [6];
^{c} from Ref. [35], values in parentheses estimated from Eq. (6)

this interaction is proportional to the square of q_H. The values of q_H calculated by a semiempirical MNDO method are collected in Tables 1 and 2 [of course, $q_H(H^+) = 1$]. The parameters $q_H > 0.15$ are typical for protic solvents as e. g. water, alcohols, and unsubstituted amides, whereas the $q_H < 0.07$ are characteristic for aliphatic aprotic ones.

It should be stressed that q_H does not correlate with electrostatic parameters defined in Part I of this paper [7]. The linear regressions of q_H with calculated dipole moments, UN and UP (c. f. Table 1 in Ref. [7]) give correlation coefficients of $r = 0.089$, 0.047, and 0.046, respectively, for $N = 89$ in all cases under study. The lack of correlation is understandable, because the electrostatic parameters should not be collinear with q_H which is a tentative measure of the hydrogen-bond-donating ability.

Using the UP and q_H values we have tried to apply them to interpret some solvent acidity scales. The decision concerning the choice of the analyzed scales is,

after all, arbitrary; therefore it is sufficient to say that we have chosen the most popular E_T and AN scales. The acceptor number, AN, introduced by Mayer et al. [4, 28] is based on the ^{31}P-NMR chemical shift in triethylphosphine oxide in the respective solvent. The electron pair acceptance polarity index of Dimroth and Reichardt [6, 29], E_T, is the lowest energy transition of the indicator solute 2,6-diphenyl-4-(2′,4′,6′-triphenyl-1-pyridino)phenoxide dissolved in the given solvent. Although not specifically designed to measure both those parameters, they are also a measure of the hydrogen-bond-donating ability of the solvent.

The significant result of our correlation analysis is the planar regression obtained for solvents number $2-5$, 8, 10, 22, 23, 25, 26, 28, 31, 38, 40, 43, $45-47$, 49, 51, 53, 57, 63, and 64 from Table 1 as well as 3, 5, 9, 11-16, and 19 from Table 2 (i.e. water excluded from the set of 35 solvents for which experimental AN values are listed in Table 1 or Table 2) in the following form

$$AN = 632\,q_\mathrm{H}^2 + 0.251\,UP + 2.5 \tag{6}$$

with $r = 0.961$ and $s_{AN} = 3.5$ ($N = 34$). On the other hand, treating the problem in terms of linear regressions, we have found that the r values are 0.908 and 0.736 for the correlations of AN against q_H^2 and AN against UP, respectively. Thus, comparison of the correlation coefficient for Eq. (6) with the r-values for the corresponding linear relationship shows a significant improvement in accuracy of the planar regression. The statistical treatment with the Fisher-Snedecor test confirms fully this finding.

The two-parameter approach can also be applied to the E_T scale. In this case (solvents number $1-8$, 10, 12, $15-19$, $21-29$, 31, 32, $34-54$, 57, 60, 61, 63, 64 from Table 1, as well as $1-19$ and 22 from Table 2) the correlation equation is as follows

$$E_T = 248\,q_\mathrm{H}^2 + 0.207\,UP + 32.4 \tag{7}$$

with $r = 0.924$ and $s = 2.7$ for the set of 72 solvents (there are 74 solvents with experimental E_T values listed in Tables 1 and 2, but water and phenol deviate strongly and, therefore, they were not included in the correlation). This r value should be compared with the values of 0.784 and 0.833 for the linear regressions of E_T against q_H^2 and UP, respectively. The F-test proves that both parameters in Eq. (7) are statistically significant.

It is then clear that the solvent acidity parameters, namely AN and E_T, can be interpreted in terms of a two-parameter approach including UP and q_H^2 molecular values computable on the basis of the MNDO method. Unfortunately, water deviates from the proposed correlations. It should be mentioned in this context that the E_T value proper for "monomeric" water (i.e. dissolved in dioxane which was found to be 56.0 [30]) is closer to the value of 51.4 predicted by Eq. (7) than to the "bulk" E_T (63.1 [6]). Therefore, the deviation seems to be related to the structure of water in liquid state. Multiple reasons may influence the observed behavior of phenol but we shall not discuss this case here.

The behaviour of the molecules with flexible geometry, as e.g. ethylenediamine and substituted ethanols, should also be mentioned. These compounds are included into regressions (6) and (7) although the computed electrostatic parameters for some of them change significantly on the rotation around single C-C bond without marked changes in total energy. This means that corresponding data should be treated as tentative only.

Conclusions

Current models of solvent-solute interactions consider the two independent and complementary approaches of long-range or non-specific (electrostatic) and short-range or specific (donor-acceptor) solvation separately. This is in line with the idea of Koppel and Palm [31] who tried to split the empirical solvent parameters into separate contributions which result from the two basic types of interactions. Sometimes this distinguishing is successfully applied in practice. Notwithstanding, it appears that in reality the differentiation between non-specific and specific salvation may be simply treated as an artifact.

It is known [1 − 4, 6] that correlations of rate and equilibrium constants with solvent acidity and basicity parameters give often a better fit than with any function of electric permittivity (ε). However, there are also sizable deviations; they are notoriously observed for the highly structured protic solvents and for low dielectric media with $\varepsilon < 10$. On the other hand, there exist linear trends between certain kinetic data and solvent acceptor numbers which also include low dielectric solvents. Mayer [32] supported the suggestion that the acceptor numbers include also contributions from long-range forces.

Several years ago Bekarek and Jurina [33] correlated E_T with ε and n, the refraction index of solvents. For a set of 40 solvents they have found a correlation coefficient of $r = 0.957$. However, this regression was not valid for many classes of solvents. It is then clear that in fact the differentiation between purely specific and non-specific salvation has no physical meaning although certain attempts have been made to extract non-specific contributions from acidity and basicity parameters [34].

Is it then possible to unify two different types of description of the solvent-solute interactions? The analysis presented in this communication emphasizes the role of molecular electrostatic potentials in acid-base interactions in solutions. Previous findings [14] that electrostatic forces are responsible for the differentiation of various basicity scales is fully justified in the light of our calculations. Moreover, a proper analysis including the UP potentials and the Mullikan charges at hydrogen atoms allows also to predict the solvent acidity parameters to some extent. Thus, an analysis of "specific" interactions should allow for electrostatic effects; this brings us closer to the unified theory of solvent-solute interactions.

Acknowledgements

Appendix

The definition of the UN parameter needs also the radius of a reference cation, R. In the previous work [7] we presented a table of the UN values based on $R = 133\,pm$. We have also computed UN with corresponding reference radii other than 133 pm, and we have found that every R from the range $100 − 200\,pm$ leads to correlation coefficients of Eq. (2) better than 0.95. This can be explained with the help of relation (3) presented in Ref. [7]. However, we were fortunate to find that the best fit of Eq. (2) could be obtained for $R = 126\,pm$, with only slight improvement over $R = 133\,pm$.

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