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The Acceptor Number — A Quantitative Empirical Parameter for the Electrophilic Properties of Solvents

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With 8 Figures

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The electrophilic properties of 34 solvents have been characterized by the Acceptor Number (AN) which has been derived from ^{31}P-n.m.r. measurements of triethylphosphine oxide dissolved in the respective solvents. Relationships are found between the acceptor numbers and the Z-values, E_T-values and Y-values, as well as the free energies of solvation of anions and the redox potentials of the hexacyanoferrate(III)—hexacyanoferrate(II) system in different solvents. The new parameter provides—together with the donor number—a useful guide in choosing the most appropriate solvent for a given reaction.

1. Introduction

According to the coordination chemical point of view many chemical reactions are primarily determined by *coordination chemical* interactions between the substrate and the solvent molecules[1]. Solvent (S) attack at a polarized substrate $\overset{\delta+}{A}—\overset{\delta-}{B}$ occurs either nucleophilically at A or electrophilically at B leading either to the formation of a molecular complex (which may be stable only in solution) with increased $A—B$ bond length or to the heterolytic fission of the bond $A—B$.

$$S \rightarrow \overset{\delta+}{A} — \overset{\delta-}{B} \rightarrow S$$

nucleophilic action (as electron pair donor)	electrophilic action (as electron pair acceptor)

$$(m + n)\, S + \overset{\delta+}{A} — \overset{\delta-}{B} \rightleftarrows [A \cdot S_n]^+ + [B \cdot S_m]^-.$$

The extent of the reaction primarily depends on the nucleophilic or (and) electrophilic properties of the solvent. Consequently, qualitative and even quantitative predictions on the thermodynamics and kinetics of the reactions are possible provided that suitable quantities are available for characterizing the nucleophilic and electrophilic properties of the solvents[1–5]. In principle, all solvents are amphoteric, i.e. they may act as nucleophiles and electrophiles simultaneously. A quantitative measure of the *nucleophilic* properties of solvents is provided by the so-called "donor number" or "donicity", DN, which has been defined as the negative ΔH-value for the 1 : 1 adduct formation between $SbCl_5$ and the solvent molecules in dilute solution of 1,2-dichloroethane[6, 7]. Unfortunately no analogous quantity could be defined for characterizing the *electrophilic* properties of solvents. The latter have been shown to differ considerably even within the group of the so-called "donor solvents"[4, 5, *]. *Thermodynamic* quantities which represent a measure of the electrophilic properties of solvents are provided by the single ion free energies of solvation of halide ions[8, 9] and the half wave potentials for the polarographic reduction of the hexacyanoferrate(III)ion[10]. Since these data are comparatively difficult to determine and are available only for a limited number of solvents it appears desirable to find suitable empirical solvent parameters which allow an easy and rapid evaluation of the electrophilic properties of the solvents. Recently various investigators have demonstrated that n.m.r. chemical shift data can be successfully used for characterizing empirically the *nucleophilic* properties of solvents. For example, linear relationships have been found between donicities and chemical shifts of ^{23}Na, ^{19}F and ^{29}Si in solutions of sodium salts, CF_3I and silanols, resp.[11–13]. No systematic measurements however have been carried out so far for determining the *electrophilic* properties of solvents. As model substrate we have finally chosen triethylphosphine oxide, which, in a nearly ideal way, fulfils the following important requirements:

a) The ^{31}P nucleus is easily accessible for n.m.r. measurements.

b) The probe nucleus is remote from the actual place of interaction, namely the basic oxygen atom thereby eliminating theoretically ill-definable contact contributions to the chemical shift values.

c) Triethylphosphine oxide is a very strong base (*DN* estimated ≈ 40). This together with the partial double bond character of the P—O bond assures a high sensitivity of the phosphorus resonance towards solvent change.

d) The interaction between solute and solvent always occurs at a

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[*] Solvents which primarily act as electron pair donors owing to the presence of atoms with lone pair electrons have been classified as "donor solvents"[7].

well defined site, namely at the oxygen atom; the remaining coordination sites of the phosphorus atom are blocked off by inert alkyl groups. The incorporation of *ethyl* groups guarantees efficient electronic shielding without steric hindrance.

e) Owing to the presence of ethyl groups, triethylphosphine oxide is sufficiently soluble in all kinds of solvents. In contrast, other phosphine oxides, are only partially soluble.

f) Triethylphosphine oxide is extraordinarily stable. No decomposition was observed after several hours even in solutions of strong protonic acids.

2. Experimental Part

N.m.r. spectra were recorded with a Jeol PS-100 spectrometer. Sample tubes were 8 mm Wilmad precision glas tubes with coaxial inner cells filled with $(C_6H_5)_2POCl$ as external reference. For each solvent chemical shifts were determined for at least 5 to 6 different concentrations, usually in the range 0.05 to 0.60 mole Et_3PO/litre. The stability of the field was controlled before and after each measurement by means of a standard solution consisting of Et_3PS dissolved in benzene (0,50 mole/l) and $(C_6H_5)_2POCl$ as external reference. For this test solution a constant ^{31}P chemical shift of -9.45 ± 0.03 ppm [versus $(C_6H_5)_2POCl$] was measured over a period of several months. All ^{31}P spectra were recorded with proton decoupling in order to obtain a maximum in accuracy and sensitivity. The chemical shift values determined versus $(C_6H_5)_2POCl$ as external reference were subsequently corrected for volume susceptibility differences. Since reliable susceptibility data are available only for a limited number of the solvents listed in table 1, volume susceptibilities were determined by an n.m.r. spectroscopic method using two different reference liquids. The results of this study and a compilation of susceptibilities for the most common nonaqueous solvents will be reported elsewhere[14].

Et_3PO, Et_3PS and $(C_6H_5)_2POCl$ were synthesized according to procedures described in the literature [15–17]. Et_3PO is very hygroscopic but can be dehydrated by repeated sublimation at room temperature in a high vacuum. The anhydrous white crystalline material melts at 51 °C.

The 1 : 1 adduct between $SbCl_5$ and Et_3PO was obtained as white crystalline precipitate on mixing stoichiometric quantities of the compounds dissolved in hexane. After recrystallization from 1,2-dichloroethane the following analytical results were obtained: Cl, found: 41,03%, P, found: 7,27%; calc. for $Et_3PO \cdot SbCl_5$: Cl 40,92%, P 7,15%.

The solvents were purified and dried by standard procedures[18]. Carefull drying is a prerequisite for obtaining reliable results. The residual water content was tested by *Karl Fischer* titration and was always below 5×10^{-4} mole water/litre. All operations were carried out in an inert gas atmosphere.

3. Results

The results of the ^{31}P chemical shift measurements of Et_3PO in 34 solvents are listed in table 1. Columns 2–7 give the chemical shifts

Table 1. ^{31}P *Chemical Shifts of* Et_3PO *in Various Solvents at Different Concentrations*

Solvent*	c [mole · litre^{-1}] — δ (ppm)						δ_∞ (ppm)	$\frac{\Delta \delta}{\Delta c}$	δ_{corr} (ppm)
hexane	0.29	0.16	0.098	0.065			1.68	—8.30	0.00
	0.76	—0.33	—0.83	—1.17					
ether	0.54	0.27	0.16	0.11	0.054		0.10	curv., neg.	—1.64
	1.03	0.67	0.42	0.27	0.11				
THF	0.56	0.28	0.17	0.11	0.056		—1.89	—0.44	—3.39
	2.14	2.06	1.97	1.93	1.91				
benzene	1.93	0.96	0.30	0.19	0.15	0.060	—1.92	—0.48	—3.49
	2.88	2.35	2.08	2.02	1.98	1.95			
CCl_4	0.43	0.25	0.19	0.12	0.078	0.049	—2.22	curv., neg.	—3.64
	3.14	2.92	2.85	2.68	2.62	2.46			
diglyme	0.61	0.30	0.18	0.12	0.061		—2.60	—0.26	—4.20
	2.78	2.67	2.66	2.62	2.60	2.60			
glyme	0.55	0.28	0.17	0.11	0.055		—2.68	—0.10	—4.35
	2.73	2.72	2.70	2.70	2.68				
HMPA	1.85	0.93	0.47	0.14	0.093	0.047	—3.06	—0.25	—4.50
	3.53	3.46	3.19	3.10	3.08	3.06			
dioxane	0.67	0.34	0.20	0.13	0.067		—3.00	—0.40	—4.59
	3.28	3.16	3.10	3.08	3.01				
acetone	0.57	0.28	0.23	0.17	0.11	0.057	—3.44	—0.14	—5.33
	3.53	3.45	3.45	3.47	3.46	3.45			
NMP	0.59	0.29	0.17	0.12	0.059		—4.18	0.10	—5.65
	4.13	4.14	4.16	4.17	4.18				
DMA	1.87	0.93	0.51	0.26	0.19	0.10	—4.21	≈ 0.00	—5.80
	4.21	4.20	4.21	4.20	4.20	4.24			

pyridine	0.53	0.26	0.16	0.11	0.053		−4.46	≈ 0.00	−6.04
	4.43	4.45	4.46	4.46	4.43				
NB	1.95	0.97	0.53	0.26	0.19	0.11	−4.72	0.11	−6.32
	4.51	4.63	4.64	4.67	4.69	4.70			
BN	1.82	0.91	0.42	0.21	0.18	0.084	−5.08	0.07	−6.61
	4.85	4.97	5.06	5.04	5.06	5.06			
DMF	2.05	1.02	0.78	0.39	0.21	0.078	−5.02	0.18	−6.82
	4.65	4.83	4.89	4.98	4.98	4.98			
DCE	0.61	0.30	0.24	0.18	0.12	0.06	−5.83	−0.03	−7.11
	5.85	5.85	5.85	5.85	5.81	5.83			
PDC	1.95	0.97	0.51	0.25	0.19	0.10	−6.25	0.15	−7.77
	5.76	6.03	6.16	6.18	6.19	6.24			
DMTF	0.67	0.34	0.20	0.13	0.067		−6.54	0.17	−8.02
	6.42	6.45	6.48	6.52	6.53				
AN	0.61	0.31	0.24	0.12	0.061		−6.28	0.28	−8.04
	6.09	6.19	6.19	6.20	6.28				
DMSO	1.81	0.91	0.37	0.19	0.18	0.075	−6.66	0.34	−8.22
	6.05	6.28	6.58	6.58	6.56	6.63			
CH_2Cl_2	0.75	0.38	0.23	0.15	0.075		−7.36	0.25	−8.67
	7.22	7.26	7.29	7.31	7.34				
NM	2.00	1.00	0.55	0.25	0.20	0.10	−6.70	0.20	−8.74
	6.29	6.54	6.56	6.67	6.68	6.69			
$CHCl_3$	0.53	0.26	0.21	0.16	0.11	0.053	−8.52	curv.,	−9.83
	8.97	8.92	8.91	8.90	8.88	8.73		neg.	
NMF	0.44	0.28	0.22	0.14	0.088	0.057	−12.02	0.30	−13.66
	11.88	11.84	11.99	11.98	11.98	11.99			
isopropyl alcohol	0.49	0.28	0.24	0.097	0.056	0.028	−12.65	0.76	−14.26
	12.28	12.43	12.45	12.58	12.62	12.64			
*Et*OH	0.48	0.24	0.18	0.096	0.069	0.048	−14.15	0.36	−15.80
	13.96	14.05	14.10	14.13	14.12	14.14			

Table 1 (continued)

Solvent *	c [mole · litre^{-1}] — δ (ppm)						δ_∞ (ppm)	$\frac{\Delta\delta}{\Delta c}$	δ_{corr} (ppm)
formamide	0.57	0.28	0.17	0.11	0.057		—15.31	0.52	—16.95
	15.01	15.17	15.19	15.25	15.28				
*Me*OH	0.39	0.28	0.19	0.14	0.078	0.056	—15.85	0.32	—17.60
	15.72	15.73	15.74	15.83	15.84	15.84			
CH_3COOH	0.49	0.24	0.15	0.097	0.048		—20.81	0.60	—22.51
	20.52	20.61	20.71	20.74	20.78				
H_2O	0.57	0.28	0.17	0.11	0.057		—22.0	0.57	—23.35
	21.66	21.85	21.83	21.90	21.97				
CF_3COOH	0.62	0.31	0.18	0.12			—43.14	0.95	—44.83
	42.55	42.77	42.99	43.05					
CH_3SO_3H	0.63	0.31	0.19	0.12	0.063		—52.28	1.36	—53.77
	51.84	51.85	51.97	52.18	52.19				
CF_3SO_3H	0.48	0.24	0.14	0.096	0.048		—53.46	0.88	—54.98
	53.17	53.22	53.38	53.38	53.66				
Et$_3$PO · $SbCl_5$	0.58	0.29	0.17	0.12	0.058		—41.30	—1.06	—42.58
in *DCE*	41.91	41.59	41.50	41.42	41.36				

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* Abbreviations used in Tables 1 and 2: *THF* tetrahydrofuran; *diglyme* diethylene glycol dimethyl ether; *glyme* ethylene glycol dimethyl ether; *HMPA* hexamethylphosphoric triamide; *NMP* 1-methyl-2-pyrrolidinone; *DMA* N,N-dimethylacetamide; *NB* nitrobenzene; *BN* benzonitrile; *DMF* N,N-dimethylformamide; *DCE* 1,2-dichloroethane; *PDC* propanediol-1,2-carbonate; *DMTF* N,N-dimethylthioformamide; *AN* acetonitrile; *DMSO* dimethyl sulfoxide; *NM* nitromethane; *NMF* N-methylformamide.

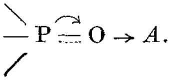
as obtained experimentally for different concentrations using $(C_6H_5)_2POCl$ as external reference. The data show that the variation of the chemical shift as a function of concentration is usually not negligible; the effect is most pronounced in hexane where δ varies by nearly 2 ppm within a concentration range of only 0.06–0.30 mole Et_3PO/litre. Since hexane is a non-polar *and* non-coordinating solvent, strong solute—solute interactions obviously occur even in dilute solutions. In general, the use of chemical shift data as empirical solvent parameters requires an extrapolation to infinite dilution! The latter values—referred to $(C_6H_5)_2POCl$—are listed in column 8. Extrapolation usually did not cause problems since in most cases δ varies linearly with the concentration. Magnitude and sign of the concentration dependence are characterized by the slope $\Delta\,\delta/\Delta\,c$, given in column 9. Non-linear relationships found for a few solvents are indicated in column 9 by "curv." and the corresponding sign. The values δ_{corr} listed in column 10 represent the chemical shift values extrapolated to infinite dilution, referred to hexane and corrected for the difference in volume susceptibilities between hexane and the respective solvents. All chemical shift values are considered to be reproducible to at least ± 0.05 ppm.

4. Discussion

4.1. Relationship between Electron Density at the Phosphorus and Electrophilic Properties of the Solvents

Table 1 contains the ^{31}P-chemical shifts of Et_3PO in different solvents. The largest shift difference observed of about 55 ppm (hexane, trifluoromethanesulfonic acid) appears to be the largest shift difference ever observed for a given compound in different solvents. As compared to hexane the resonance signals observed in other solvents are generally shifted to lower fields corresponding to a reduction of electron density at the phosphorus atom. The largest negative shifts occur in protonic acids. Large negative shifts—though smaller than in protonic acids—are observed for the hydroxylic solvents and solvents containing "acidic" C—H hydrogen atoms such as CH_2Cl_2, $CHCl_3$, formamide or N-methylformamide. Numerically smaller shift values are obtained for aprotic solvents; even then the shifts cover a range (hexane, *NM*) of nearly 9 ppm.

The influence of the nature of the solvent on the ^{31}P chemical shifts results from the polarization of the P—O bond induced by the interaction of the electrophile A with the oxygen atom. Reduction in π bond character is probably accompanied by a polarization of the σ bond, both effects leading to a decrease in electron density at the phosphorus which is related to the strength of interaction.



$$>\mathrm{P}=\mathrm{O}\rightarrow A.$$

In solutions of protonic acids HX one has generally to assume an equilibrium between the hydrogen bonded complex [I] and the fully protonated phosphine oxide [II].

$$\underset{[\mathrm{I}]}{Et_3\mathrm{PO}\rightarrow \mathrm{H}X} \rightleftharpoons \underset{[\mathrm{II}]}{[Et_3\mathrm{POH}]^+} + X^-.$$

The fact that only one resonance signal is observed is due to a rapid exchange reaction between the two species, the observed resonance signal being the weighted average of the signals of the isolated species. Despite differences in acid strengths (Table 2) nearly the same shift values were measured for the two strongest acids, namely methanesulfonic and trifluoromethanesulfonic acid, suggesting that Et_3PO is nearly exclusively present in the fully protonated form [II]. In weak protonic acids (e.g. acetic acid), in solutions of alcohols and CH acidic solvents (CH_2Cl_2, $CHCl_3$, formamide, *NMF*) the predominant species are most probably the hydrogen bonded complex [I] and uncoordinated phosphine oxide. This interpretation is in agreement with the considerable line broadening observed in trifluoroacetic acid solutions, which has an acid strength intermediate between those of acetic acid and methane- or trifluoromethanesulfonic acid, resp. (Table 2). In trifluoroacetic acid both hydrogen bonded adduct and protonated phosphine oxide appear to be present in comparable quantities. The exchange process is sufficiently rapid to give a single resonance signal, but is slow enough to cause line broadening. In all other solvents sharp resonance lines are observed.

The comparison of table 1 and table 2 shows that (with the exception of acetic acid) there is a correlation between chemical shift and pK_a values. The deviation observed for acetic acid is almost certainly due to the strong association in the liquid state, by which the effective acceptor strength of this solvent is reduced. The chemical shift values found for the alcohols and CH-acidic solvents agree with the order of increasing acceptor strength in the series $CH_2Cl_2 < CHCl_3 <$ isopropyl alcohol $< Et\mathrm{OH} < Me\mathrm{OH} < H_2O$, as obtained by spectroscopic measurements[19, 20]. Within the group of aprotic solvents, hexane (and other saturated hydrocarbons) as expected behave as extremely poor electrophiles. Surprisingly benzene and carbon tetrachloride which are nonpolar and considered as inert solvents show definitely stronger electrophilic properties than the polar diethyl ether. This may explain the formation of "pentahalocarbonate" complexes from carbon tetrachloride and tetraalkylammonium halide[22]. The extremely weak electrophilic properties of ether solvents which would not be expected from a consideration of their dipole moments, account for the high reactivity of bases (e.g. carbanions) in these media and hence for the usefulness of these solvents for electrophilic substitution reactions[33]. Ketones behave also as comparatively weak electrophiles. The electrophilic character of carboxylic acid amides varies over a broad range. Solvents which are capable of hydrogen bonding such as formamide or N-methylformamide show acidities similar to the lower aliphatic alcohols. Substitution of acidic hydrogen atoms by alkyl groups drastically decreases the electrophilic properties, the shift difference for formamide and *DMA* being approximately 11 ppm. Well developed electrophilic properties are exhibited within the group of dipolar aprotic solvents by *DMSO*, *AN* and *PDC*. The fact that these solvents at the same time possess appreciable nucleophilic properties and fairly high dielectric constants (Table 2) accounts for their increasing use in basic research chemistry and industry. Hexamethylphosphoric triamide is a particularly interesting solvent. According to Table 2 it is a very poor electrophile but an extraordinarily strong donor. These unique properties together with a comparatively high dielectric constant make it particularly suitable as a medium for reactions involving strong and highly reactive bases such as alkoxides, carbanions etc. The combination of these properties of *HMPA* also accounts for the observation that (as in liquid ammonia) alkali metals dissolve with formation of comparatively stable blue colored solutions containing "free" electrons and strongly solvated metal ions[23]. The fact that this reaction does not proceed in ethers is due to their much weaker donor properties (see Table 2). Nitromethane, in contrast to *HMPA*, shows well developed electrophilic but only poor nucleophilic properties.

In order to characterize the electrophilic properties of solvents it appears appropriate to introduce a new dimensionless quantity, which is proportional to the observed chemical shift values δ_{corr}. In view of the definition of the "Donor Number" DN as a measure of the *nucleophilic* properties of a solvent we propose to refer the chemical shift values δ_{corr} of Table 1 to the chemical shift value δ_{corr} of the 1 : 1 Et_3PO—$SbCl_5$ adduct dissolved in 1,2-dichloroethane (see Table 1) which is arbitrarily taken as 100. The values thus obtained may be termed "*Acceptor Numbers*", AN, and represent a measure of the *electrophilic* properties of the solvents*. The "Acceptor Numbers" are obtained from the shift

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* The symbol AN should not be confused with the abbreviation used for the solvent acetonitrile.

Table 2. *Acceptor Numbers (*AN*), Donor Numbers (*DN*), Dielectric Constants* ε, *Dipole Moments* μ, *Kosowers Z-values, Dimroth—Reichardts* E_T *Values, Winstein—Grunwalds Y-values and* pK_a*-values for Various Solvents at 25 °C (for Abbreviations for Solvents see Footnote of Table 1)*

Solvent	No.	AN	DN	ε	μ [*Debye*]	*Z* [kcal/mole]	E_T [kcal/mole]	*Y*	pK_a
hexane	1	0.0		1.9	0.0		30.9		
ether	2	3.9	19.2	4.2	1.25		34.6		
THF	3	8.0	20.0	7,4	1,7	58.8	37.4		
benzene	4	8.2	0.1	2.3	0.0	54.0	34.5		
CCl_4	5	8.6		2.2	0.0		32.5		
diglyme	6	9.9							
glyme	7	10.2		7.0		59.1	38.2		
HMPA	8	10.6	38.8	29.6	5.37	62.8	40.9		
dioxane	9	10.8		2.2	0.4		36.0		
acetone	10	12.5	17.0	20.7	2.88	65.6	42.2		
NMP	11	13.3	27.3	33.0	4.1		42.2		
DMA	12	13.6	27.8	37.8	3.81	66.9	43.7		
pyridine	13	14.2	33.1	12.3	2.2	64.0	40.2		
NB	14	14.8	4.4	34.8	4.0		42.0		
BN	15	15.5	11.9	25.2	3.9	65.0	42.0		
DMF	16	16.0	26.6	36.7	3.86	68.4	43.8	—3.470	
DCE	17	16.7		10.1	1.75	63.4	41.9		
PDC	18	18.3	15.1	65.0	4.98		46.6		
DMTF	19	18.8							

AN	20	18.9	14.1	36.0	3.44	71.3	46.0		
DMSO	21	19.3	29.8	46.7	3.90	71.1	45.0		
CH_2Cl_2	22	20.4		8.9	1.5	64.7	41.1		
NM	23	20.5	2.7	36.7	3.57	71.2	46.3		
$CHCl_3$	24	23.1		4.7	1.1	63.2	39.1		
NMF	25	32.1		182.4	3.8		54.1		
i-propyl alcohol	26	33.5		18.3	1.7	76.3	48.6	−2.730	18
*Et*OH	27	37.1		24.3	1.7	79.6	51.9	−2.033	18
formamide	28	39.8		109.5	3.4	83.3	56.6	0.604	
*Me*OH	29	41.3	19.0	32.6	1.71	83.6	55.5	−1.090	16
CH_3COOH	30	52.9		6.2	1.3	79.2	51.2	−1.675	4.7
H_2O	31	54.8	18.0	78.5	1.8	94.6	63.1	−3.493	15.7
CF_3COOH	32	105.3							−0.26
CH_3SO_3H	33	126.3							−1.20
CF_3SO_3H	34	129.1							$\ll -1.20$
$Et_3PO \cdot SbCl_5$ in *DCE*		100.0							

values δ_{corr} listed in Table 1 according to equation (1) and they are presented in Table 2.

$$\mathrm{AN} = \frac{\delta_{\mathrm{corr}}}{\delta_{\mathrm{corr}}\,(\mathrm{SbCl_5} \cdot Et_3\mathrm{PO})} \times 100 = \delta_{\mathrm{corr}} \times 2{,}348 \qquad [1]$$

4.2. Relationship between Acceptor Number and Other Empirical Solvent Parameters

4.2.1. Basic Considerations

A number of empirical solvent parameters have been proposed as a measure of "solvent polarity" or "solvent ionizing properties"*, such as *Kosowers* "Z"-values[25], the "E_T"-values of *Dimroth* and *Reichardt*[26] and the "Y"- and "log k_1"-values of *Winstein* et al.[27, 28]. In several cases it is possible to correlate spectral, thermodynamic and kinetic data by use of these empirical parameters[29, 30]. On the other hand there are many examples of solvent dependent processes, such as the formation of metal ion complexes[31], the ionization of organometallic substrates[32, 33], the formation of molecular adducts[34] and many redox reactions[35], which cannot be correlated to any of these parameters. This is due to the fact, that no clear distinction between nucleophilic and electrophilic contributions to solute—solvent interactions has been made in determining solvent parameters. A more close consideration shows that solvent parameters such as Z-values or E_T-values neither represent a general measure of the polarity nor of the ionizing properties of the solvents[33]. The frequent use of the terms "solvent polarity" and "ionizing power" as synonymous expressions[29] is particularly unfortunate and misleading. As has been shown in a number of previous review articles[1–5, 21] (compare also Table 2) no general relationship exists between solvent polarity (that is the dipolar character of the solvent molecules—or more precisely, the distribution and polarizability of the charges) and ionizing properties (that is the ability of the solvent to heterolyse covalent bonds). The *ionizing* properties of the solvents primarily depend on their coordination chemical properties, i.e. their nucleophilic and (or) electrophilic properties. The ionizing properties of a given solvent towards a given substrate to be heterolysed may vary considerably with its actual function displayed: it may function as an electron pair donor or as an electron pair acceptor or it may exercise both functions at the same time[1–5, 21]. It is therefore apparent, that a successful and general application of empirical solvent parameters is only possible if a suitable model substrate (such as Et_3PO) is chosen, which is indicative for a specific solvent function.

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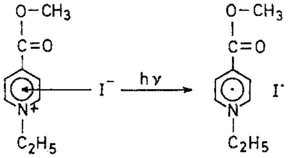
* A comprehensive survey on empirical solvent parameters has been given by *Reichardt*[24].

4.2.2. Z-, E_T- and Y-Values

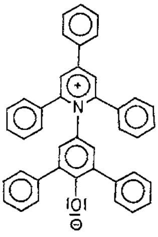
Kosower[25] proposed the so-called Z-value as a measure of "solvent polarity" which represents the energy of the charge transfer band of the 1-ethyl-4-carbomethoxypyridinium iodide ion pair [III]:



[III] [IV]

As has been supposed from the structure of the ion-pair[33], the Z-values show a definite relationship to the electrophilic properties of the solvents (Fig. 1). Interaction of the ground state [III] with the solvent occurs primarily by electrophilic attack at the iodide ion, the cation being coordinatively saturated. As a consequence of electron transfer to the pyridinium system coordination chemical and electrostatic interactions necessarily play only a minor role for the stabilization of the excited state [IV]. Fig. 1 reveals the existence of an approximately linear relationship between acceptor numbers and Z-values for solvents with dielectric constants above 10. For solvents with lower dielectric constants the Z-values generally exhibit negative deviations indicating that dielectric polarization effects become important owing to the highly polar character of the ground state complex. In this way the low Z-value of acetic acid as compared to water may be explained: H_2O : $\varepsilon = 78{,}5$, $AN = 54{,}8$. CH_3COOH : $\varepsilon = 6{,}2$, $AN = 52{,}9$.

Similar relationships are found if the E_T-values are plotted versus the acceptor numbers (Fig. 2). The former represent the energy of the lowest electronic transition of the pyridinium-N-phenol betaine [V]. Although [V] is a neutral compound with a large π-electron system



[V]

its behaviour is expected to be very similar to that of the pyridinium iodide [III]. Solvent attack again occurs electrophilically at the highly basic oxygen atom which is sterically fairly well accessible while the nitrogen is again coordinatively saturated.

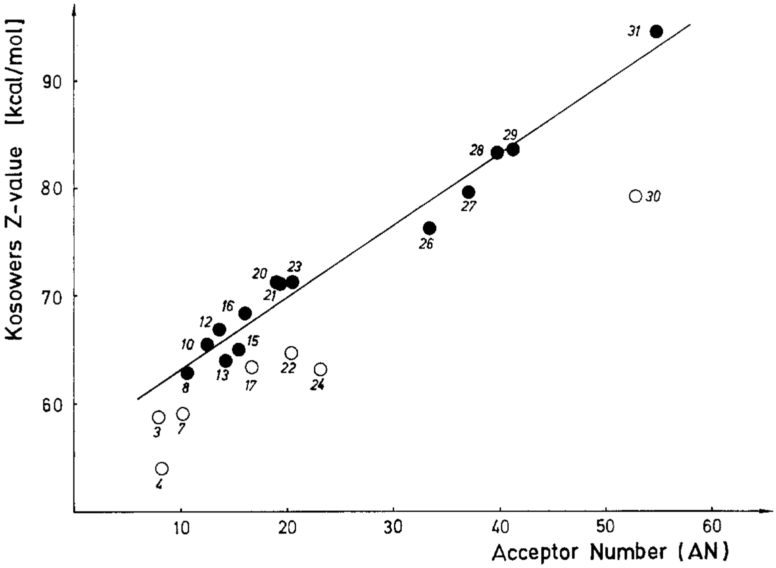


Fig. 1. Relationship between Acceptor Numbers and *Kosowers* Z-values

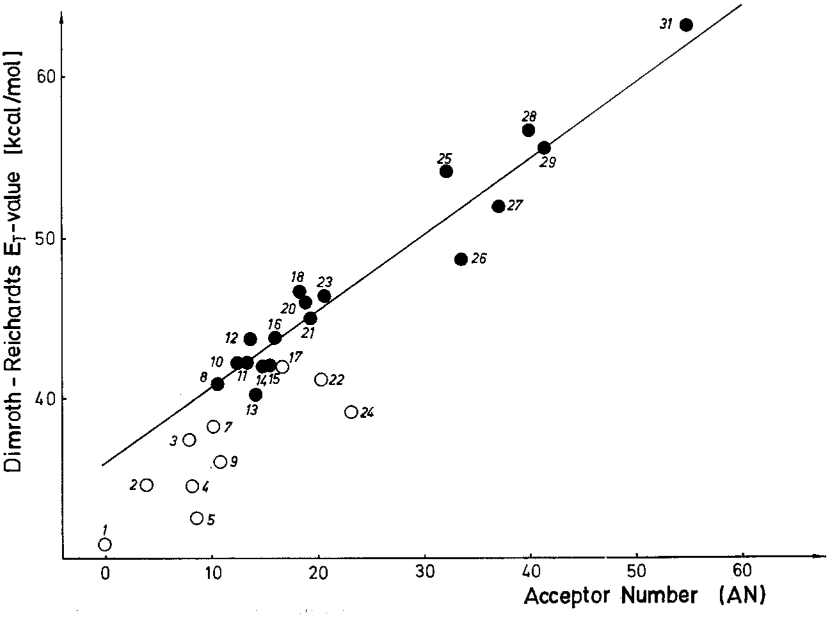


Fig. 2. Relationship between Acceptor Numbers and *Dimroth—Reichardts* E_T-values

A close relationship also exists between the acceptor numbers and the so-called "Y"-values of *Winstein* und *Grunwald*[27]. The "Y"-values are defined by equation (2)

$$Y \equiv \log \frac{k^S}{k^{S0}} \qquad [2]$$

where k^S and k^{S0} denote the first order rate constants for the solvolysis

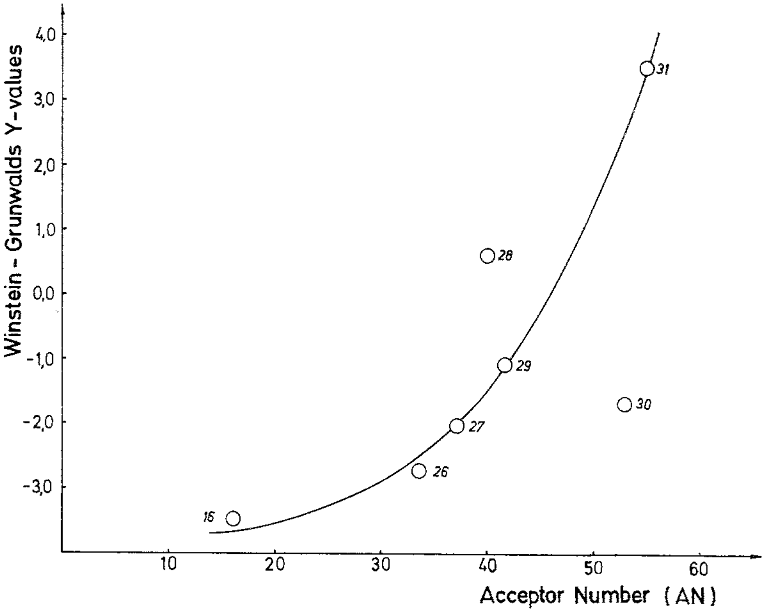


Fig. 3. Relationship between Acceptor Numbers and *Winstein—Grunwalds* Y-values

of t-butyl chloride in a solvent S and the standard solvent S^0 (EtOH : H_2O = 4 : 1 by volume). A complex [VI]

$$R_3C^{\oplus} \leftarrow X^{\ominus}$$

[VI]

with a highly polar C—X bond may be considered for the transition state. Since the tertiary carbon atom is usually strongly shielded towards solvent attack, stabilization of the transition state will essentially depend on the interaction with the halide ion, i.e. on the electrophilic properties of the solvent. A plot of Y-values versus acceptor numbers (Fig. 3) shows, that the former are in fact increasing with increasing AN-values. Two significant deviations are observed: similar to fig. 1, the rate in acetic acid ($\varepsilon = 6.2$) is much slower than expected, while the reaction is strongly accelerated in formamide ($\varepsilon = 109.5$). In view of the relatively high donor strength of the latter (DN $\approx$ 23, estimated) and the favourable size of the molecule, this phenomenon probably partly results from an additional stabilization of the transition state by simultaneous nucleophilic attack at the carbon atom (pushpull mechanism). The possible occurance of such a mechanism in the solvolysis of tertiary alkyl halides has already been pointed out by *Ross* and *Labes*[36]. The use of "*Y*"-values for practical purposes is rather limited since (with the exception of *DMF*) reliable values are available so far only for a few hydrogen bonding solvents and several mixtures thereof[37]. Attempts to correlate various other empirical solvent parameters such as Ω-, *F*-, δ-values, etc. (see footnote on page 1246) with acceptor or donor numbers, were usually unsuccessfull. Obviously, most of these parameters reflect the variable influence of different solvent properties on the processes investigated.

4.3. Relationship between Acceptor Numbers, Thermodynamic Solvation Quantities and Solvent Dependent Processes

In view of thermodynamic calculations, relationships between empirical solvent parameters and thermodynamic solvation quantities are particularly interesting. Free energies of solvation of various halide ions have been determined, mainly by *Parker* et al.[8, 9], and have been successfully used (together with the solvent donicities) for the precalculation of thermodynamic and kinetic data of various equilibria[5, 38]. Fig. 4 shows that a functional relationship exists between acceptor numbers and the free energies of solvation of the chloride ion. This offers an opportunity for the convenient and rapid estimation of free energies of solvation which are rather difficult to determine by experiment. A similar although less rigorous correlation exists (Fig. 5) between acceptor numbers and the half wave potentials for the polarographic reduction of hexacyanoferrate(III) to hexacyanoferrate(II), which represent an alternative measure of the electrophilic properties of solvents[10]. In Figs. 4 and 5 a *free energy* quantity is related to chemical shift data which most closely reflect the *enthalpy* of interaction between Et_3PO and the solvent molecules. Deviations observed may therefore be due to variable entropy contributions.

By applying acceptor numbers predictions may be made on the courses of many reactions which are predominantly influenced by the *electrophilic* properties of the solvents. The relationship which exists between acceptor numbers and rates of solvolysis of tertiary alkyl halides has already been mentioned in the preceding section. In Fig. 6

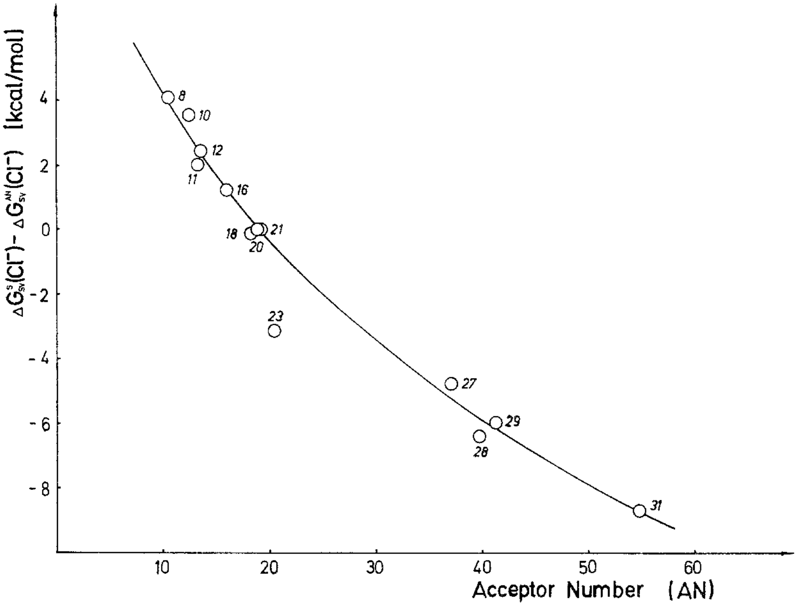


Fig. 4. Relationship between Acceptor Numbers and free energies of solvation of the chloride ion referred to the solvent acetonitrile. Data $\Delta G_{\mathrm{SV}}(\mathrm{Cl}^-)$ from ref.[5]

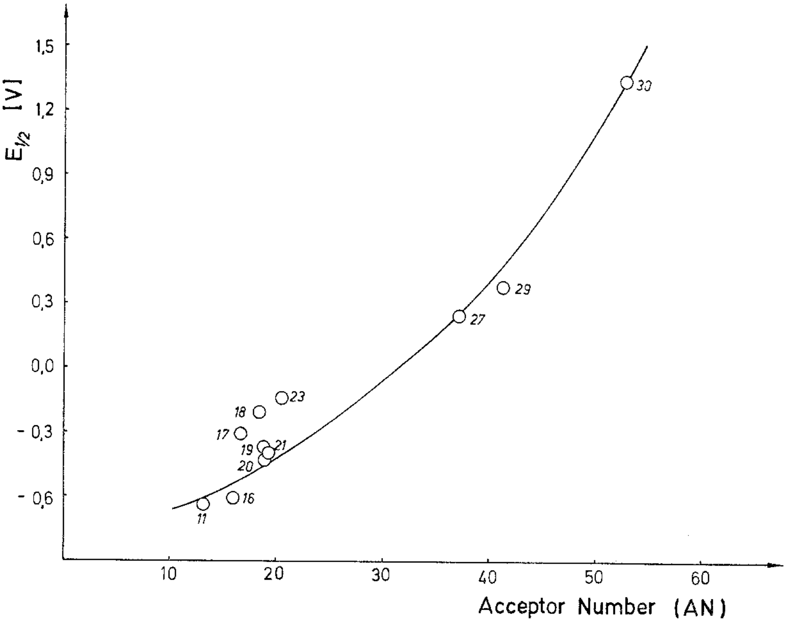


Fig. 5. Relationship between Acceptor Numbers and half wave potentials for the reduction of $[Bu_4N]_3[Fe(CN)_6]$ in $0{,}1M$-Bu_4NClO_4-solution [referred to bisdiphenylchromium(I)iodide]. Data $E_{1/2}$ from ref.[10]

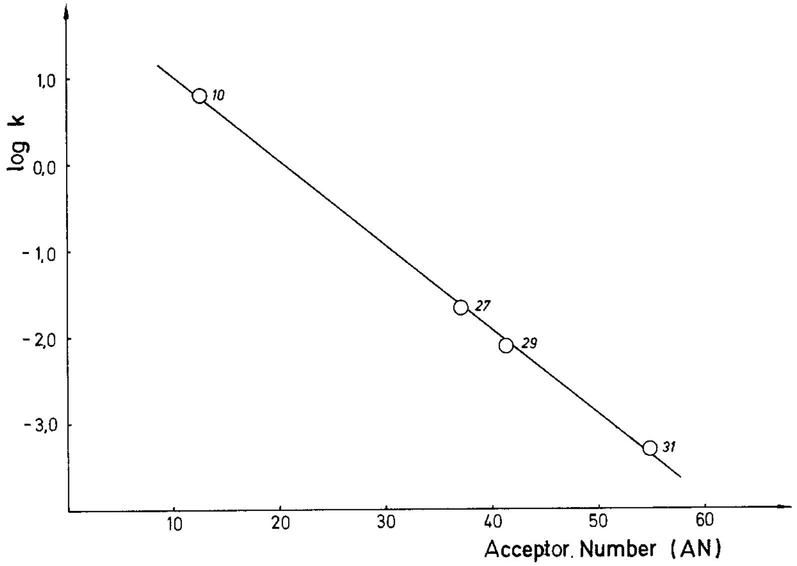


Fig. 6. Relationship between Acceptor Numbers and logarithms of the second order rate constants for the reaction of CH_3I with radioactive iodide ions. Kinetic data from ref.[39]

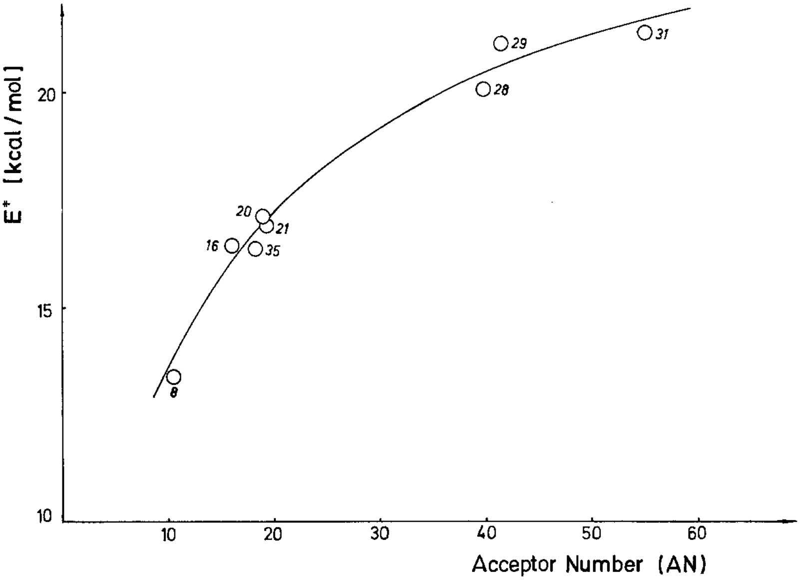


Fig. 7. Relationship between Acceptor Numbers and *Arrhenius* activation energies for the reaction of n-butylbromide with azide ions. Kinetic data from ref.[40]. Solvent No. 35: ethyleneglycol carbonate

acceptor numbers have been correlated with the logarithms of the second order rate constants for the reaction of methyl iodide with labelled iodide ions[39]:

$$CH_3I + {}^*I^- \rightarrow CH_3I^* + I^-.$$

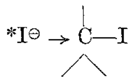
Tabelle 3. *Transition Energy for the π—π^* Transition of Mesityl Oxide in Various Solvents*

Solvent	ΔE [kcal/mole]
isooctane	123.98
AN	122.23
DCE	121.30
isopropyl alcohol	121.04
*Et*OH	120.94
CH_3OH	120.73
H_2O	117.85

Table 4. *Transition Energies ΔE for Visible Absorption Bands of* $[IrBr_6]^{2-}$ *in Various Solvents*

Solvent	ΔE [kcal/mole] band III	 band IV$_b$
pyridine	47.02	52.56
acetone	47.10	52.65
DCE	47.33	53.24
$CHCl_3$	47.49	53.54
NM	47.81	53.64
CH_3OH	47.97	54.56
H_2O	49.04	56.17

Since the donor strength of the iodide ion in the transition state complex [VII] is lower than that of the free ion,



[VII]

the starting products are increasingly stabilized (as compared to the transition state) with increasing "accepticity" of the solvent. As a consequence the reaction rates decrease with increasing acceptor number.

An excellent correlation was also found between acceptor numbers and the *Arrhenius* activation energies for the reaction of n-butyl bromide with azide ions (Fig. 7) which also proceeds via an S_N2 mechanism[40]. Rough correlations exist also between acceptor numbers and various spectroscopic quantities such as the π—π* transition energy of mesityl oxide[29] (Table 3) or the transition energies of the visible absorption bands of the hexabromoiridate(IV) anion[41] (Table 4).

Particularly noteworthy is the relationship which exists between acceptor numbers and the ^{13}C chemical shifts in the $\rangle C{=}O$-group of acetone determined by *Maciel* and *Natterstad*[42] in various solvents. The general trend (Fig. 8) is a shift of the ^{13}C resonance signals to lower field with increasing acceptor number, indicating an increasing polarization of the C=O double bond. The sensitivity to solvent change is much lower than is found for *Et*$_3$PO; irregularities are presumably due to the fact, that the sp^2 hybridized carbon atom is less shielded towards contact interactions than is the phosphorus atom in *Et*$_3$PO.

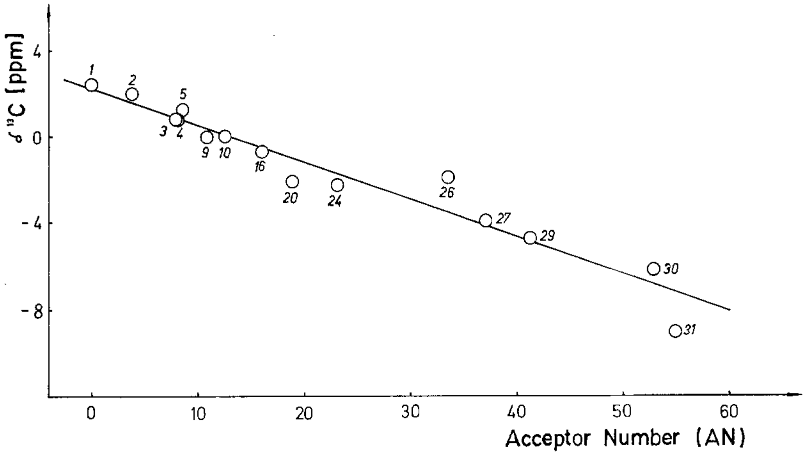


Fig. 8. Relationship between Acceptor Numbers and $^{13}C{=}O$ chemical shifts of acetone. ^{13}C chemical shifts from ref.[42]

5. Summary and Conclusion

Based on the ^{31}P chemical shifts of triethylphosphine oxide measured in solution, a new quantity has been defined, the so-called acceptor number (AN) which represents a quantitative and sensitive measure for the electrophilic properties of solvents. Owing to the unique solubility properties of *Et*$_3$PO, acceptor numbers are available for all types of coordinating and noncoordinating solvents. The availability of acceptor numbers in addition to the previously defined donor number[1, 6] now allows a separate characterization of the electrophilic and nucleophilic properties, resp. of the solvents. As has been shown for a few selected reactions[5], it seems possible to evaluate semiquantitatively or even quantitatively the solvent influence on the thermodynamics and kinetics of many reactions.

Solvent dependent processes which are primarily influenced by the electrophilic properties of solvents, such as substitution reactions of primary alkyl halides, have been correlated with the acceptor numbers.

The approximate relationships found between acceptor numbers and various empirical solvent parameters, namely the Z-values of *Kosower*, the E_T-values of *Dimroth—Reichardt* and the Y-values of *Winstein—Grunwald* provide an understanding of the physical-chemical significance of these parameters. Apparently Z-, E_T- and Y-values most closely (but not exclusively) represent a measure of the *electrophilic* properties of the solvents and therefore necessarily fail when applied to reactions which are influenced or mainly controlled by the *nucleophilic* properties of the solvents.

Close relationships have been found to exist between acceptor numbers and thermodynamic quantities such as the free energies of solvation of halide ions[8, 9] or the redox potentials of the hexacyanoferrate(III)—hexacyanoferrate(II) system[10]. Such relationships are important for estimating thermodynamic quantities (needed for thermodynamic calculations) by simple n.m.r. measurements.

The results of this study suggest that acceptor numbers are particularly useful in characterizing the acidities of hydrogen bonding solvents and protonic acids which otherwise may be difficult to obtain.

Several years ago it was discovered that many standard organic reactions proceed much faster in dipolar aprotic than in conventional hydroxylic solvents or solvent mixtures[43–46]. It is obvious that this phenomenon is due to the high reactivity of the bases involved in these reactions in solvents of low acceptor numbers. Acceptor numbers are therefore particularly important for the organic chemist, since they provide a quantitative measure of the reactivity of bases such as halide ions, alkoxides or carbanions in a given solvent. The consideration of both donor and acceptor numbers provides a guide in choosing the most appropriate solvent for a special synthetic problem.

Work is in progress to determine acceptor numbers for aqueous—nonaqueous and nonaqueous—nonaqueous solvent mixtures. This data will hopefully give a better insight into preferential solvation phenomena and will be particularly interesting for the interpretation of kinetic results available in mixed solvents. Apart from that we intend to test the use of anionic bases such as the fluoride ion or the phosphate ion as alternative probes for the electrophilic properties of solvents.

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References

[1] *V. Gutmann*, Chemische Funktionslehre. Wien-New York: Springer. 1971.

[2] *V. Gutmann*, Topics in Current Chem. **27**, 59 (1972).

[3] *V. Gutmann* and *R. Schmid*, Coord. Chem. Rev. **12**, 263 (1974).

[4] *U. Mayer* and *V. Gutmann*, Advan. Inorg. Chem. Radiochem. **17**, 189 (1975).

[5] *U. Mayer*, Pure Appl. Chem. **49**, 291 (1975).

[6] *V. Gutmann* and *E. Wychera*, Inorg. Nucl. Chem. Lett. **2**, 257 (1966).

[7] *V. Gutmann*, Coordination Chemistry in Non-aqueous Solutions. Wien-New York: Springer. 1968.

[8] *R. Alexander*, *A. J. Parker*, *J. H. Sharp*, and *W. E. Waghorne*, J. Amer. Chem. Soc. **94**, 1148 (1972).

[9] *B. G. Cox*, *G. R. Hedwig*, *A. J. Parker*, and *D. W. Watts*, Austral. J. Chem. **27**, 477 (1974).

[10] *V. Gutmann*, *G. Gritzner*, and *K. Danksagmüller*, Inorg. Chim. Acta (in the press).

[11] *R. H. Erlich* and *A. I. Popov*, J. Amer. Chem. Soc. **93**, 5620 (1971).

[12] *P. Spaziante* and *V. Gutmann*, Inorg. Chim. Acta **5**, 273 (1971).

[13] *E. A. Williams*, Presented at the 9th Organosilicon Symposium in Cleveland, Ohio, April 5, 1975, private communication.

[14] *W. Gerger*, *U. Mayer*, and *V. Gutmann*, in preparation.

[15] *F. Hein* and *H. Hecker*, Chem. Ber. **93**, 1339 (1960).

[16] *A. Cahours* and *A. W. Hofmann*, Ann. Chem. **104**, 23 (1857).

[17] *E. L. Gefter*, Zhur. Obsh. Khim. **28**, 1338 (1958); Chem. Abstr. **52**, 19999d.

[18] *J. A. Riddick* and *W. B. Bunger*, Techniques of Chemistry (*A. Weissberger*, ed.), Vol. II. New York-Toronto: Wiley-Interscience. 1970.

[19] *A. Balasubramanian* and *C. N. R. Rao*, Spectrochim. Acta **18**, 1337 (1962).

[20] *T. Olsen*, Acta Chem. Scand. **24**, 3081 (1970).

[21] *U. Mayer* and *V. Gutmann*, Structure and Bonding **12**, 113 (1972).

[22] *J. A. Creighton* and *K. M. Thomas*, J. Chem. Soc., Dalton Trans. **1972**, 403.

[23] *H. Normant*, Angew. Chem. **79**, 1029 (1967).

[24] *Ch. Reichardt*, Lösungsmittel-Effekte in der organischen Chemie. Weinheim: Verlag Chemie. 1969.

[25] *E. M. Kosower*, J. Amer. Chem. Soc. **80**, 3253 (1958).

[26] *K. Dimroth*, *Ch. Reichardt*, *T. Siepmann*, and *F. Bohlmann*, Ann. Chem. **661**, 1 (1963).

[27] *E. Grunwald* and *S. Winstein*, J. Amer. Chem. Soc. **70**, 846 (1948).

[28] *S. G. Smith*, *A. H. Fainberg*, and *S. Winstein*, J. Amer. Chem. Soc. **83**, 618 (1961).

[29] *E. M. Kosower*, J. Amer. Chem. Soc. **80**, 3261, 3267 (1958).

[30] *Ch. Reichardt* and *K. Dimroth*, Topics in Current Chem. **11**, 1 (1968/69).

[31] *U. Mayer* and *V. Gutmann*, Mh. Chem. **101**, 912 (1970).

[32] *V. Gutmann* and *U. Mayer*, Mh. Chem. **100**, 2048 (1969).

[33] *V. Gutmann*, Coord. Chem. Rev., submitted for publication.

[34] *V. Gutmann*, Coord. Chem. Rev. **15**, 207 (1975).

[35] *V. Gutmann*, Structure and Bonding **15**, 141 (1973).

[36] *S. D. Ross* and *M. M. Labes*, J. Amer. Chem. Soc. **79**, 4155 (1957).

[37] *A. H. Fainberg* and *S. Winstein*, J. Amer. Chem. Soc. **78**, 2770 (1956).

[38] *U. Mayer*, Mh. Chem., to be published.

[39] *E. R. Swart* and *L. J. Le Roux*, J. Chem. Soc. **1957**, 406.

[40] *J. J. Delpuech*, Tetrahedron Letters **25**, 2111 (1965).

[41] *Ch. K. Jørgensen*, J. Inorg. Nucl. Chem. **24**, 1587 (1962).

[42] *G. E. Maciel* and *J. J. Natterstad*, J. Chem. Phys. **42**, 2752 (1965).

[43] *D. J. Cram*, *B. Rickborn*, *C. A. Kingsbury*, and *P. Haberfield*, J. Amer. Chem. Soc. **83**, 3678 (1961).

[44] *J. Miller* and *A. J. Parker*, J. Amer. Chem. Soc. **83**, 117 (1961).

[45] *A. J. Parker*, J. Chem. Soc. **1961**, 1328.

[46] *A. J. Parker*, Advances in Physical Organic Chemistry (*V. Gold*, ed.), Vol. 5, p. 173. London-New York: Academic Press. 1967.

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