

Re-interpretation of the Solvent Dielectric Constant in Coordination Chemical Terms

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It is found for common aprotic solvents that the logarithm of the dielectric constants can be represented by a linear combination of the acceptor numbers (AN) and the donor numbers (DN) (or equivalent parameters),

$$\log \epsilon = c_1(AN) + c_2(DN) + c_3$$

With this equation, concepts of specific and non-specific solvation are brought under the umbrella of one treatment. The equation does not hold for the highly structured solvents. For these, the dielectric constants predicted on the basis of the acceptor and donor numbers are orders of magnitude larger than the experimental values, revealing how poorly the associates are dissociated by the macroscopically attainable electric fields.

KEY WORDS: Dielectric constant; empirical solvent parameters; associated solvents; solvent-reactivity correlations.

1. INTRODUCTION

There are few topics in chemistry in which so many misunderstandings and controversies have arisen as in the issue of characterizing and scaling the solvating power of solvents. Above all, the relevance of the dielectric constant to chemical activity in solution has remained a bone of contention. Here, the subject is reviewed from a historical point of view.

The first solvent property applied to correlate reactivity data was the dielectric constant in the form of dielectric functions, summarized elsewhere,⁽¹⁾ as suggested from elementary electrostatic theories. Though work during the last two decades has tended to downgrade the

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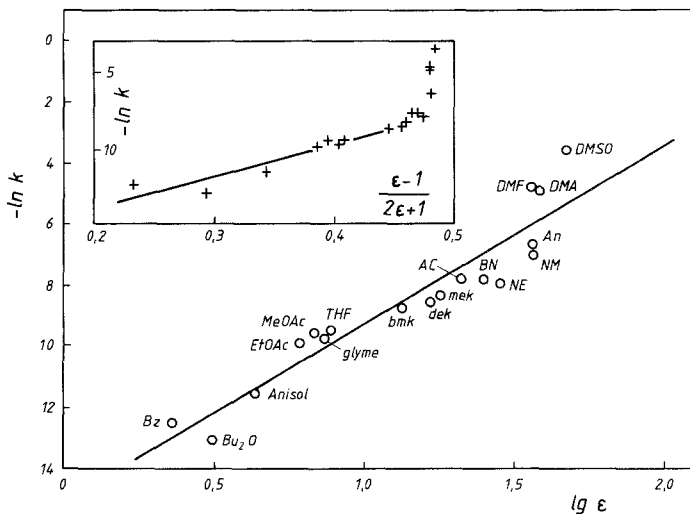


Fig. 1. Relationship between the second-order rate constant at 50°C of the reaction of *p*-nitrofluorobenzene with piperidine and the solvent dielectric properties [data are from Ref. (2)]. (For abbreviations of the solvents in this figure and the following figures see Table I.)

usefulness of the dielectric approach, there are correlations that *have* succeeded. An example is shown in Fig. 1 and refers to the S_N2 reaction of *p*-nitrofluorobenzene with piperidine.⁽²⁾ The classical dielectric functions predict decreasing importance of the dielectric constant of the solvent as its dielectric constant increases such that reactivity changes are not allowed in solvents of dielectric constant above approximately 30. For instance, the Kirkwood function has an upper limiting value of 0.5, with the value of 0.47 at $\epsilon=25$. The insert in Fig. 1 illustrates this point. Insignificantly better is the Clausius-Mosotti function as it has an upper limiting value of unity. The $\log \epsilon$ function, however, is without a limiting value at all and is therefore to be preferred if high dielectric solvents are included.

Because of the often observed inadequacies of the dielectric approach the problem of correlating solvent effects was next tackled by applying empirical parameters. This strategy revealed two outstanding properties of a solvent, namely the donor (nucleophilic, basic, cation-solvating) and acceptor (electrophilic, acidic, anion-solvating) abilities implying that solute-solvent interactions can be considered as acid-base reactions in the broadest possible sense. The majority of the solvents used are essentially amphoteric with no relationship being found

between the donor and acceptor strengths. Certainly the description of solvent effects as a linear function of these two independent but complementary parameters proved to be a cornerstone in the evolution of solvent-reactivity correlations.^(3,4)

Correlations of rate and equilibrium data with empirical parameters invariably give a better fit than with any function of solvent dielectric constant. Nevertheless there are also sizable deviations from the straight-line relationships. The majority of the notoriously deviating solvents can be numbered among two classes of solvents, namely (i) the highly structured or associated solvents and (ii) the low dielectric solvents with dielectric constants of below 10. The former will be dealt with in more detail later on. We just anticipate that, as a rule, protic and aprotic solvents should not be mixed in a correlation analysis for the sake of physical relevance of the latter.

Current models of solvent-solute interactions consider the two approaches – the dielectric and that based on empirical parameters – as complementary viewpoints⁽¹⁾ and differentiate between electrostatic and coordination chemical solvation. Accordingly, the free energy of solvation is considered as consisting of the sum of two terms which stem from the donor-acceptor interactions between solute and solvent in the immediate vicinity of the solute ('short-range' or 'hydrogen-bonding type' interaction, 'specific' solvation) and beyond that sphere, from the dielectric polarization of the solvent ('long-range' interaction, 'unspecific' or 'Born type' solvation).⁽⁵⁾

Concerning the deviations for the low dielectric solvents Parker *et al.*⁽⁴⁾ have suggested that the donor-acceptor concept may not extend to that type of solvents. Support of this idea comes from studies of Fowler *et al.*⁽⁶⁾ who reported considerable improvements in correlating solvent effects when combining Dimroth-Reichardt's E_T values (which are thought to reflect the specific solvation) with a dielectric function (which is thought to represent the non-specific solvation). It must be mentioned, however, that the inclusion of a dielectric function term as a *third* term, in addition to solvent donor and acceptor terms, does not generally improve correlations.⁽⁵⁾ On the other hand, there are linear trends between certain kinetics data and solvent acceptor numbers which also include low dielectric solvents, so that Mayer⁽⁵⁾ was led to the suggestion that the acceptor numbers possibly include contributions from long-range forces. This would be in line with the ideas of Koppel and Palm⁽¹⁾ who tried to split the empirical solvent parameters into separate independent contributions which stem from the two basic types of solute-solvent interactions.

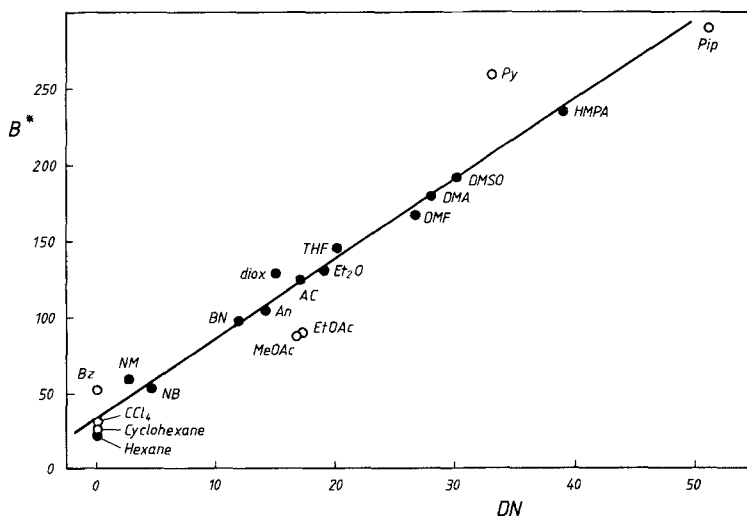


Fig. 2. Relationship between the Lewis basicity parameter $B^{(1.8)}$ and donor numbers. Solvents labelled by full circles have been used to calculate Eq. (1).

However, distinguishing between long-range and short-range forces is not very successful in practice. It appears to the present author that the question concerning a relationship between the dielectric constant and the coordination chemical properties of a solvent is still up for discussion. An important corollary to the underlying problem comes from the close relationship between the donor number DN and the Lewis basicity parameter B scales (see Fig. 2), as the former is obtained in dilute dichloroethane solution (implying that electrostatic contributions are evidently constant), whereas the latter stems from measurements performed with 0.4M solutions of CH_3OD in the neat solvents. Thus, specific and non-specific interaction changes parallel each other, or, heretically, traditional electrostatic solvation – as a counterpart to specific solvation – does not exist at all or else is insignificant.

In the following discussion we shall show that in fact the differentiation between specific and non-specific solvation is a mere artifact with no physical relevance. For this purpose it is at first necessary to refine the large number of empirical parameters.

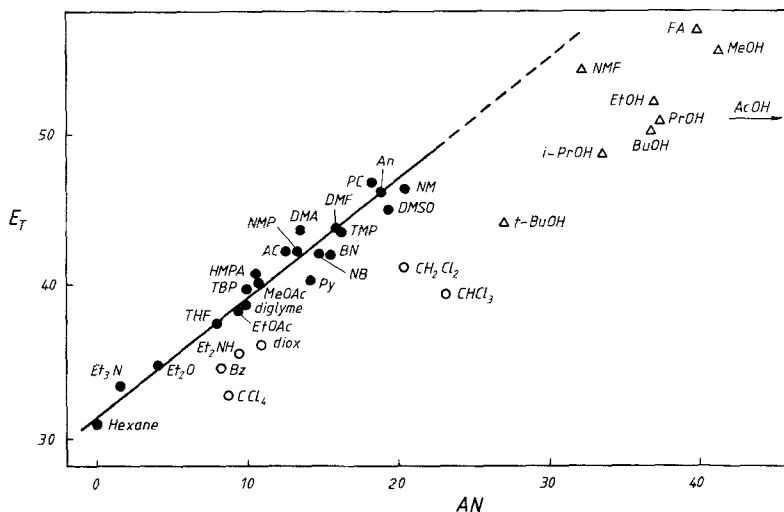


Fig. 3. Relationship between the E_T values⁽¹⁰⁾ and the acceptor numbers. Solvents labelled by full circles have been used to calculate Eq. (2). Δ , highly structured solvent.

2. REFINING THE EMPIRICAL SOLVENT PARAMETERS

The fundamental requirement is to adopt parameters based on model substrates which allow a separate characterization of the nucleophilic and electrophilic solvent properties. We here choose the donor numbers (DN) and the acceptor numbers (AN) of Gutmann's school⁽⁷⁾ because of the simple structure of the respective reference compounds, antimony pentachloride and triethylphosphine oxide. There are other more or less equivalent scales, viz. the donor number scale is in close agreement with the Lewis basicity parameter $B^{(7,8)}$ (Fig. 2), the standard free energies of transfer of the potassium cation, $\Delta G_{tr}(K^+)$,⁽⁴⁾ and the ^{19}F chemical shift of trifluoroiodomethane,⁽⁹⁾ etc. Further, linear trends are found between the acceptor number scale and e.g. the Dimroth-Reichardt E_T values⁽¹⁰⁾ (Fig. 3), the Kosower Z values⁽¹¹⁾ and the free energy of transfer of the chloride ion, $\Delta G_{tr}(Cl^-)$.⁽⁴⁾

We have in addition introduced DN_B and AN_E values.⁽¹²⁾ The former are based on the equation

$$DN_B = -6.36 + 0.19 B^* \quad (1)$$

as derived by means of a linear regression analysis using 13 solvents

Table I. Classification of Solvents by the Donor Number, Acceptor Number, and Dielectric Constant

Solvent	<i>DN</i>	<i>DN_B^a</i>	<i>AN</i>	<i>AN_E^{b,c}</i>	ϵ ^d
Acetic acid (AcOH)		10.5	52.9	(25.7)	6.2
Acetic anhydride (Ac ₂ O)	10.5			16.2	20.7 (19 ^o)
Acetaldehyde (AcH)		18.9 ^e	13.4 ^f		21.1 (21 ^o)
Acetone (AC)	17.0	17.0	12.5	14.0	20.7
Acetonitrile (An)	14.1	13.2	18.9	18.9	36.0
Acetophenone		14.1		12.9	17.4
2-Aminoethanol			33.7	(26.4)	37.7
Aniline		33.3		16.7	6.9
Anisole		7.9		7.6	4.3
Benzaldehyde		13.6	12.8 ^f		17.8 (20 ^o)
Benzene (Bz)	0	3.5	8.2	4.1	2.3
Benzonitrile (BN)	11.9	12.0	15.5	13.8	25.2
Benzylcyanide	15.1			14.9	18.7 (27 ^o)
Bromobenzene (BrBz)		2.2		8.0	5.4
<i>n</i> -Butanol (BuOH)	≥20	24.0	36.8	(24.4)	17.5
<i>t</i> -Butanol (<i>t</i> -BuOH)	≥20		27.1	(16.2)	12.5
Butanone (mek)		14.3		12.9	17.9
Carbon disulfide (CS ₂)	<5			1.6	2.6
Carbon tetrachloride (CCl ₄)	(0)	0	8.6	1.5	2.2
Chloroform (CHCl ₃)	(0)	0	23.1	10.0	4.7
Chlorobenzene (ClBz)	(0)	2.2		8.0	5.6
Cyclohexane	(0)	0		0	2.0
Cyclohexanone		18.7		12.2	18.3 (20 ^o)
Di- <i>n</i> -butyl ether (Bu ₂ O)		18.1		2.6	3.1
1,2-Dichloroethane (DCE)	(0)	2.9	16.7	13.6	10.1
Dichloromethane (CH ₂ Cl ₂)	(0)	1.2	20.4	12.6	8.9
Diethylamine (Et ₂ NH)	≥50		9.4	5.2	3.7
Diethylene glycol dimethyl- ether (diglyme)			9.9	9.4	
Diethyl ether (Et ₂ O)	19.2	18.1	3.9	4.2	4.2
Dimethoxyethane (glyme)	20	17.0	10.2	8.8	7.2
Dimethylacetamide (DMA)	27.8	27.4	13.6	15.0	37.8
3,3-Dimethylbutanone (bmK)		12.0		10.5	13.2
Dimethylformamide (DMF)	26.6	25.1	16.0	16.1	36.7
Dimethylsulfoxide (DMSO)	29.8	30.1	19.3	17.6	46.7
1,4-Dioxane (diox)	14.8	18.0	10.8	6.0	2.2

Table I. Continued

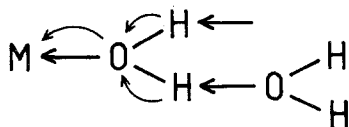
Solvent	DN	DN_B^a	AN	$AN_E^{b,c}$	ϵ^d
Epichlorhydrin (Epi)		12.0		12.0	22.6 (22°)
Ethanol (EtOH)	$\sim 20^i$	(6.5)	37.1	(26.6)	24.3
Ethylacetate (EtOAc)	17.1	10.9	9.3	8.7	6.0
Ethylamine (EtNH ₂)	55	52.2	(4.8) ^f		6.2
Ethylenediamine (en)	55		20.9		12.9
Ethylpropionate (EtOPr)		8.7 ^e	6.7 ^f		5.6 (19°)
Formamide (FA)	24		39.8	(32.6)	109.5
Formic acid (HCOOH)			83.6		57.9 (20°)
Furan		4.3	3.3 ^f		2.9
Hexamethylphosphoric triamide (HMPA)	38.8	38.1	10.6	12.3	29.6
Hexane	(0)	0		0	1.9
Methanesulfonic acid			126.3		
Methanol (MeOH)	$\sim 19^i$	(12)	41.3	(31.2)	32.6
Methylacetate (MeOAc)	16.5	10.3	10.7	11.2	6.7
N-Methylformamide (NMF)	27		32.1	(29.4)	182.4
N-Methyl-2-pyrrolidinone (NMP)	27.3		13.3	14.0	33.0
Nitrobenzene (NB)	4.4	3.7	14.8	13.8	34.8
Nitroethane (NE)		5.0		15.8	28.5
Nitromethane (NM)	2.7	4.8	20.5	19.3	36.7
3-Pentanone (dek)		12.6		10.3	16.6
Piperidine (Pip)	51	48.7		5.4	5.8 (22°)
Phosphorous oxichloride	11.7		11.0 ^f		13.0
<i>n</i> -Propanol (PrOH)	≥ 20		37.3	(25.0)	20.3
<i>i</i> -Propanol (<i>i</i> -PrOH)	≥ 20		33.5	(22.3)	18.3
Propylene carbonate (PC)	15.1		18.3	19.7	65.0
Propionitrile (PN)	16.1	13.4		16.0	27.2 (20°)
Pyridine (Py)	33.1	43.0	14.2	11.5	12.3
Sulfolane (TMS)	14.8		19.2		43.3 (30°)
Tetrahydrofuran (THF)	20.0	20.6	8.0	7.8	7.5
Tetramethylurea (TMU)	31			12.5	23.4
Toluene (To)		3.9		3.3	2.4

Table I. Continued

Solvent	DN	DN_B^a	AN	$AN_E^{b,c}$	ϵ^d
Tri- <i>n</i> -butyl phosphate (TBP)	23.7		9.9	10.7	7.9 (30 ⁰)
Triethylamine (Et ₃ N)	61	53.5	1.4	2.5	2.4
Trifluoroacetic acid	0 ^h		105.3		8.2
Trifluoroethanol	0 ^g		53.5	(36.4)	26.7 (20 ⁰)
Trifluoromethane sulfonic acid	0 ^h		129.1		
Trimethylphosphate (TMP)	23.0		16.3	15.8	20.6 (20 ⁰)
Water (H ₂ O)	18 ⁱ	17.0 (19.5) ^g	54.8	(41.0)	78.4
Xylene (mixed isomers)		4.8		2.4	2.3

^a Calculated from the B^* or B values^(1,8) using Eq. (1). ^b Calculated from the E_T values (Ref. 10) using Eq. (2). ^c Values in parentheses refer to highly structured solvents.

^d Solvent dielectric constant at 25°C, except when indicated. ^e Calculated from a linear relationship between $\Delta\nu_D^{(13)}$ and DN . ^f Estimated from values of DN and ϵ according to the equation, $AN = -2.33 - 0.056 DN + 12.73 \log \epsilon$. ^g Estimated from $\Delta G_r(K^+)$, Ref. (4). ^h We expect values similar to CF₃CH₂OH, *i.e.* close to zero. ⁱ For highly structured solvents, particularly for water, methanol, and ethanol the term bulk donicity, *i.e.* the donor number of the solvent in the associated liquid, haunts the literature.^(10,14-16) It was introduced because of the desire to rationalize the deviations for the above solvents in the plots of the ²³Na-NMR chemical shifts^(17,18) and ESR parameters⁽¹⁹⁾ vs. the donor numbers. As the basic donor numbers were measured in an inert diluent, they reflected the donor ability of the isolated solvent molecule. In the neat liquid an increase in the donor ability should occur owing to the outer-sphere complex formation:



In other words, we are dealing with solvated solvent molecules. Though it is safe to assume that this process is really taking place, we don't believe that thereby the effective donor numbers are increased by as much as is claimed (the bulk donicities are said to be, for water=33, for MeOH=25.7, and for EtOH=31.5). We would tentatively suppose for the changes to be in the range of a few donor number units only and thus to be within the usual uncertainties.

distinguished by the full circles in Fig. 2. An analogous AN_E scale has been derived for 21 solvents (filled circles in Fig. 3), yielding,

$$AN_E = -40.52 + 1.29 E_T$$

In this way the best-known scales are expressed in one form.

The first purpose of this treatment is to reveal the reliability of the individual values in that greater generality is expected when the AN (DN) and AN_E (DN_B) are in close agreement. Table I now gives a comprehensive compilation of these solvent properties as well as the dielectric constants for common pure solvents.

3. A UNIFYING APPROACH

An inspection of the data in Table I shows that the low dielectric solvents fall into the following three classes:

1. Solvents of negligible AN or DN (the saturated hydrocarbons),
2. Solvents of small AN and high DN (some amines) or medium DN (the ethers), and
3. Solvents of small DN and moderate AN (the partially chlorinated hydrocarbons).

An increasing dielectric constant would bring us to solvents which possess both properties appreciably. At the other end of the scale we arrive at *N*-methylformamide, a solvent of both excellent donor and acceptor abilities. The same would be the case for *N*-methylacetamide the solvent with the highest dielectric constant so far known. The trend of these properties advocates the dielectric constant to be a measure of the amphoteric character of solvents. This idea is borne out in that $\log \epsilon$ can be represented as a linear combination of the donor and acceptor numbers by the following regression equation

$$\log \epsilon = 0.0711(AN_E) + 0.0054(DN_B) + 0.2581 \quad (3)$$

We used the AN_E and DN_B values of the following 31 solvents (abbreviations are from Table I) Ac_2O , AC , An , AP , Anisole, BN , mek , cyclohexane, cyclohexanone, Bu_2O , Et_2O , glyme, DMA , bmK , DMF , $DMSO$, Epi , $HMPA$, hexane, NB , NE , NM , dek , Pip , PC , PN , TMS , THF , TUM , TBP , and TMP . Thus, we eliminated those solvents which cause marked deviations from the linear relationships in the plots of E_T vs. AN (Fig. 3) and B^* vs. DN (Fig. 2) and likewise chemically similar solvents which cannot be compared owing to the lack of data.

The correlation coefficient for Eq. (3) is $R=0.957$. For our 28

Table II. Calculated and Experimental Dielectric Constants
for Various Solvents ^a

Solvent	ϵ_{calc}	ϵ_{exp}	Solvent	ϵ_{calc}	ϵ_{exp}
Ac ₂ O	29.3	20.7	DMF	34.6	36.7
AC	22.2	20.7	DMSO	47.1	46.7
An	47.1	36.0	diox	6.0	2.2
Acetophenone	17.9	17.4	Epi	15.0	22.6
Aniline	42.3	6.9	EtOAc	8.6	6.0
Anisole	6.9	4.3	HMPA	21.8	29.6
Benzene	3.7	2.3	Hexane	1.8	1.9
BN	20.2	25.2	MeOAc	12.9	6.7
Benzylcyanide	25.1	18.7	NMP	25.2	33.0
Bromobenzene	6.9	5.4	NB	18.2	34.8
mek	17.9	17.9	NE	25.6	28.5
CS ₂	2.5	2.6	NM	45.3	36.7
CCl ₄	2.3	2.2	dek	11.4	16.6
CHCl ₃	9.3	4.7	Pip	8.1	5.8
Chlorobenzene	6.9	5.6	PN	29.7	27.2
Cyclohexane	1.8	2.0	PC	55.0	65.0
Cyclohexanone	16.9	18.3	Py	20.4	12.3
Bu ₂ O	3.5	3.1	TMS	50.5	43.3
DCE	17.4	10.1	THF	8.4	7.5
CH ₂ Cl ₂	14.5	8.9	TMU	20.7	23.4
Et ₂ NH	7.9	3.7	Toluene	3.3	2.4
Et ₂ O	4.5	4.2	TBP	14.0	7.9
glyme	9.5	7.2	Et ₃ N	5.3	2.4
DMA	29.7	37.8	TMP	32.1	20.6
bmk	11.7	13.2	Xylene	2.8	2.3
Highly Structured Solvents					
	ϵ_{calc}	ϵ_{exp}		ϵ_{calc}	ϵ_{exp}
AcOH	139	(11900)			6.2
<i>n</i> -BuOH	133	(1010)			17.5
<i>t</i> -BuOH	33	(196)			12.5
en		(110)			12.9
EtOH	181	(1009)			24.3
FA	508	(1651)			109.5
MeOH	379	(1982)			32.6
NMF	312	(486)			182.4
<i>n</i> -PrOH	139	(1043)			20.3
<i>i</i> -PrOH	89	(560)			18.3
CF ₃ COOH		(6 × 10 ⁷)			8.2
CH ₃ CH ₂ OH	701	(1 × 10 ⁴)			26.7
Water	1864	(2 × 10 ⁴)			78.4

^a For abbreviations see Table I. ^b Calculated from AN_E values, in parentheses from AN .

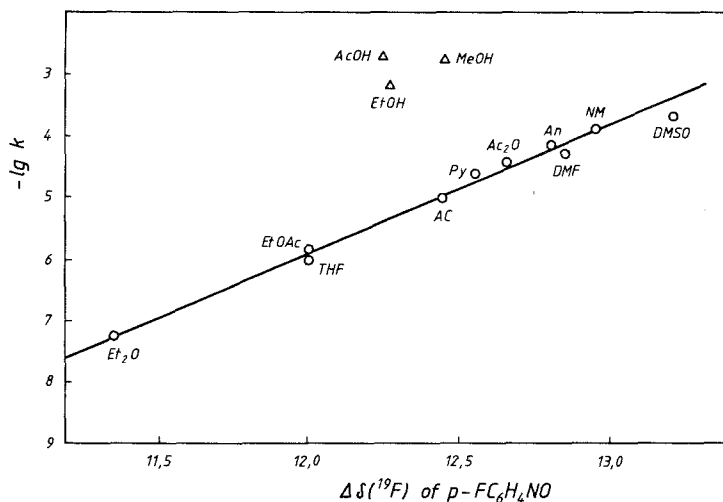


Fig. 4. Relationship between the solvent-dependence of the solvolysis rate of *p*-methoxyneophyl tosylate and the ^{19}F chemical shift of *p*-nitrosfluorobenzene [from Ref. (25)]. Δ , highly structured solvents.

degrees of freedom (31 minus 3), this would correspond to a *t*-value of 17.5. Thus, the hypothesis of no-correlation must be rejected at the practically 100% probability level ($\alpha < 10^{-13}$). In Table II the calculated and experimental dielectric constants for most of the solvents included in Table I have been listed. Even the calculated values for the solvents excluded from the analysis are not so bad (apart from that of the highly structured solvents).

3.1. Highly Structured Solvents

At first, the invalidity of the equation for the highly structured solvents should be emphasized. Actually the dramatic deviations for these solvents from the requirements of Eq. (3) would recommend the present analysis to be physically sensitive. The point is that these deviations are caused by the same properties as those that cause the protic solvents to not obey the solvent-reactivity correlations obtained for aprotic media. Highly structured solvents may not act as donors or acceptors unless the bonds between the solvent molecules are broken the extent of which in turn depends on the donor and acceptor strengths of the solute. Consequently, the coordination chemical properties of these solvents would not appear to be constant, but rather to

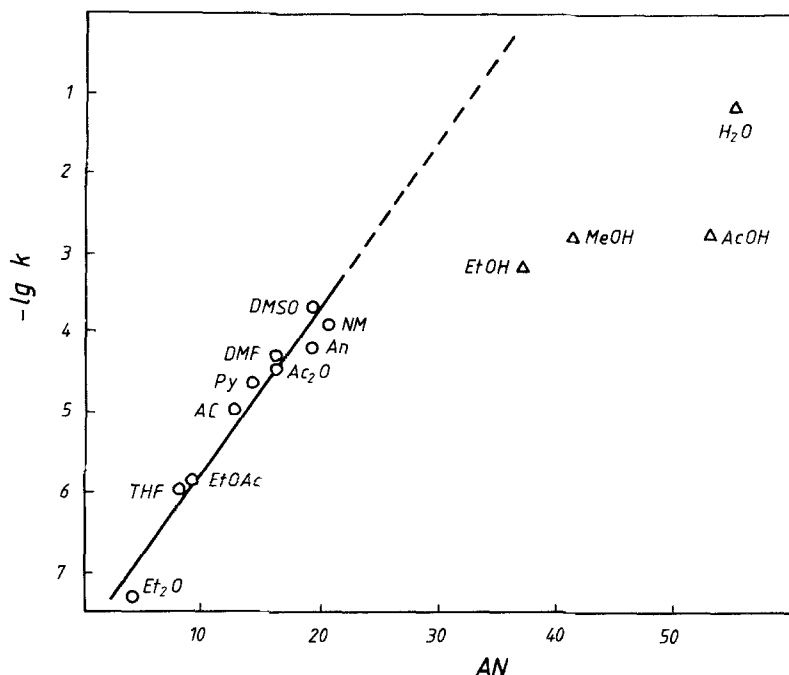


Fig. 5. Relationship between the solvent-dependence of the solvolysis of *p*-methoxyneophyl tosylate and the acceptor numbers (from Ref. (5)). Δ , highly structured solvents.

be functions of the complimentary solute properties. Experimental evidence in favor of this interpretation is afforded by the contrast of Figs. 4 and 5. In the former, the solvent-dependence of the rate of solvolysis of *p*-methoxyneophyl tosylate, which is the reaction used to define the $\log k_1$ indices,⁽²⁰⁾ is plotted vs. the shift of the ¹⁹F-NMR signal for *p*-nitrosofluorobenzene⁽²¹⁾ in the same solvents. Both processes are predominantly affected by the solvent acceptor abilities, as is revealed by their relations to the acceptor numbers.^(5,7) (The rate of the solvolysis is governed by the solvation of the developing tosylate anion.) The plot of $\log k$ vs. *AN* is shown in Fig. 5. The conspicuous difference between the plots in these figures is the direction of the deviations for the structured solvents as they come to fall above and below the line. As regards the relative strength of the acceptors involved, it is safe to assume that they are in the order



Therefore the solvolysis rate of the tosylate in question, in structured solvents, is faster than one would predict from the chemical shift of *p*-nitrosofluorobenzene on the one hand, but, on the other, is slower than predicted from the acceptor numbers. Since the reference compounds of *DN* and *AN* scales exhibit the strongest coordination chemical properties of the indices of the common scales (SbCl_5 is a stronger acceptor than either CH_3OH and K^+ , and Et_3PO is a stronger donor than Cl^- and the model substrates for the E_{T} and Z values), it is clear that the highly structured liquids would deviate from the linear inter-correlation diagrams in the direction of higher acceptor and donor numbers, respectively (see *e.g.* Fig. 3). Similar deviations usually occur in the solvent-reactivity correlations. This is to be expected, since the solvent-dependence of any $\log k$ values are related essentially to differences between initial and transition state polarities. Therefore the solvation power of the highly structured solvents, for practical purposes, is not well measured by donor and acceptor numbers. In the special event that the substrate under consideration exhibits similar coordination chemical properties to the model substrate of the solvent scale used, structured solvents may no longer fall off-line. The correlation between Z and E_{T} values is even improved on including the protic solvents.⁽¹⁰⁾

Changing now to the dielectric approach, the electrically charged plates of a condenser can be considered by far as the most poorly solvatable reference system owing to the small macroscopically attainable fields. Thus, the former poorly dissociate the associates of highly structured liquids so that the orientational polarization does not properly reflect the coordination chemical power inherent in the molecules. It can be seen that the discrepancies between calculated and experimental dielectric constants are considerably larger when using the basic *AN* scale than that based on E_{T} .

3.2. Sensitivity Coefficients

The sensitivity coefficients of Eq. (3) prompt comment because the effect of the donor strength is much less pronounced than one would expect from the suggestion that ϵ measures the amphoteric property of the solvents. However, small as it is, this effect appears to be physically significant, as can be seen from a consideration of HMPA and DMSO, two solvents of excellent donor ability. If we drop the donor number term in Eq. (3), HMPA would have a dielectric constant of 13.6 instead of 21.8 ($\epsilon_{\text{exp}} = 29.6$), and for DMSO the value would be

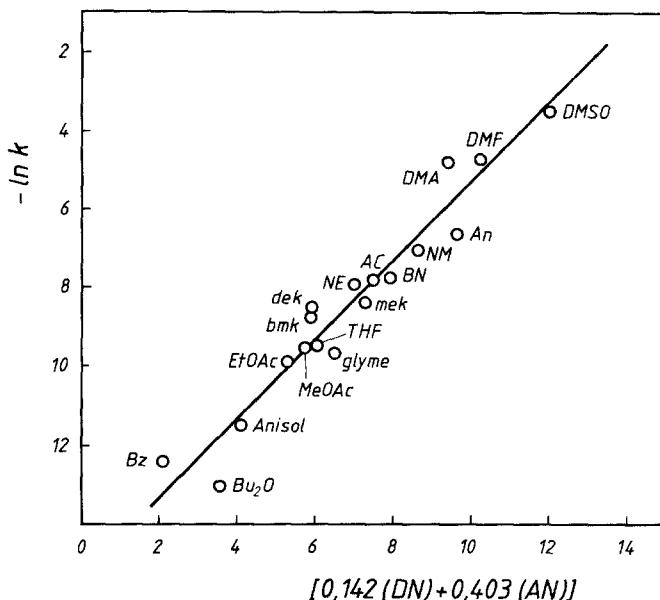


Fig. 6. Correlation diagram for the same reaction series as in Fig. 1.

32.3 instead of 47.1 ($\epsilon_{\text{exp}} = 46.7$). Compared to that, a one-parameter approach which allows only for AN_E would give, for the same 31 solvents, the equation,

$$\log \epsilon = 0.32 + 0.073(AN_E)$$

with $R=0.950$, $s=0.129$. For this, HMPA would possess $\epsilon=16.6$ and DMSO, $\epsilon=40.6$.

The small donor number effect in Eq. (3) could reflect the peculiar molecular structure of the common dipolar aprotic solvents. Negative charge is localized on oxygen or nitrogen which is situated at the periphery of the molecule. In contrast, positive charge is not localized but rather smeared over a number of hydrogens bound to carbon. To a first approximation (and neglecting the effect of varying distances of charge-separation which can upset the rule) the greater that number, the smaller the acceptor properties and likewise the dielectric constant. In other words, any good acceptor is also a good donor, but not vice versa. This feature can be invoked to account for the considerably greater weight of the acceptor number over the donor number term in Eq. (3). The solvents other than oxygen or nitrogen donors, namely

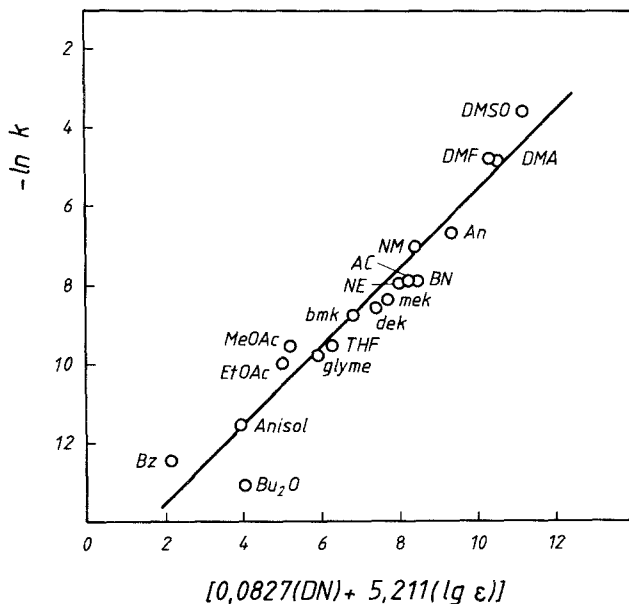


Fig. 7. Correlation diagram for the same reaction series as in Fig. 1.

the chlorine-donors (the chlorinated hydrocarbons) and the aromatic solvents (*i.e.*, π -donors) show the relative largest discrepancies between calculated and experimental values of the dielectric constant. (Clearly these discrepancies are larger when using AN instead of AN_E values.) It is worth noting that the same solvents often deteriorate solvent-reactivity correlations as well as the interrelationships of empirical solvent parameters (*e.g.* in Fig. 3).

The observations made so far imply that Eq. (3) is not generally valid for the liquid state but only for the commonly used solvents due to the similarities in their molecular structure. The limitations are obvious when considering sulfur-donors, *i.e.*, soft solvents. For instance, *N,N*-dimethylthioformamide (DMTF) has a higher dielectric constant (47.8) than DMF (36.7), whereas the acceptor properties are similar (18.8 and, 16.0 respectively) and the donor properties depend strongly on the reference compound: the DN values, suggested from $\Delta G_{tr}(K^+)$ are 1.2 and 26.6, whereas from $\Delta G_{tr}(Ag^+)$, they are 52.6 and 25.7, respectively.⁽¹²⁾

4. CONCLUSIONS

The dielectric constant is a good guide to solvent influence for reaction series which are controlled predominantly by the acceptor properties of the solvents involved. The same solvents (*e.g.* benzene) and similar ones (*e.g.* toluene and xylene), deviating in Fig. 3, would likewise deviate in the plots of $\log k$ vs. $\log \epsilon$. Therefore the quality of the correlations will depend strongly on the choice of solvents. This means that care is necessary when interpreting such correlations with respect to the occurrence or the absence of solvent acceptor effects.

The limits of the dielectric approach are reached as the solvent donor effect comes into play. Concerning this point, it seems reasonable to interpret the deviations for DMF, DMA, and DMSO in Fig. 1 by assuming that the dielectric constant does not sufficiently reflect the high donor numbers of these solvents. This is in agreement with the results of a multiple regression analysis which reveals some balanced effects of both the solvent donor and acceptor properties (Fig. 6). Finally, the dielectric approach will fail completely for reaction series involving predominant solvent donor effects. This interpretation prompts a re-consideration of the successful treatments reported which combine dielectric functions with chemical parameters. These then turn out to be nothing else but allowing for the complimentary solvent property. As an example, the reader may recognize the improvements in going from Fig. 1 to Fig. 6 and compare them with Fig. 7. In this case, $\log \epsilon$ represents the contribution of an acceptor effect. Likewise, the occasional success of the combination of E_T values and the dielectric functions, quoted above, may be rationalized similarly. On this basis it is also clear why the addition of a dielectric function term as a third parameter to donor and acceptor number terms, on the whole, fails to improve the correlations. In fact the physical picture of solvent effects is not advanced, but on the contrary confused, by the procedure.

Thus we see that the occasional deviations of the low dielectric solvents from the linear relationships may not be rationalized in terms of an electrostatic solvation. There must be other reasons. The most reasonable explanation is that in solvents with very feeble acidic and basic properties, the reference compounds for the solvent scales or the starting material of the reaction system to be studied will prefer self-association and thereby simulate solvation interactions. These effects, in the author's opinion, form in addition to the highly structured solvents the second conceptual difficulty in the application of empirical

solvent parameters. Often, however, the low dielectric solvents may deteriorate the relationships simply because of an improper correlation analysis, for instance on mixing protic and aprotic solvents in the correlation diagrams. (cf. Fig. 4 in Ref. 4 and Fig. 5 in Ref. 5).

Finally, the question that is raised concerns a theoretical explanation of the $\log \epsilon$ function.^(22,23) It transpires that the classical dielectric functions may be valid only for very low polarity systems, but break down for appreciably polar solvents due to the failure of the 'structureless continuum' model for the solvent. The reason is that the dipolar solvent-solute interaction would result in local order of the solvent around the solute because of 'solvent freezing.' To account for this dielectric saturation, Block and Walker⁽²⁴⁾ modified the basic Onsager theory for a dielectric and thereby arrived at a complex logarithmic function of ϵ of the form (see also Ref. 25),

$$f(\epsilon) = \frac{3\epsilon \log \epsilon}{\epsilon \log \epsilon - \epsilon + 1} - \frac{6}{\log \epsilon} - 2 \quad (4)$$

which the reaction field depends on. From this a theoretical explanation of $\log \epsilon$ results namely, that within an experimentally relevant ϵ range between 2 (hexane) and 70 (PC), $\log \epsilon$ varies fairly linearly with $f(\epsilon)$.

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