A SEMIEMPIRICAL MODEL FOR THE DESCRIPTION OF SOLVENT EFFECTS ON CHEMICAL REACTIONS

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Abstract — An attempt is made to provide a more rigorous basis for the description of solvent effects on chemical reactions by taking into account the various free energy contributions involved in the transfer of a substrate from the gas to the solution phase. It is shown that the solvent influence on various chemical and physical processes can be represented in a semi-quantitative or even quantitative way by means of three parameters, namely the socalled acceptor number, which represents a measure of the electrophilic or acceptor properties of the solvent, the donor number, which represents a measure of the nucleophilic or donor properties of the solvent and the standard free energy of vaporization of the solvent which is related to the free energy required to create holes in the solvent in which the substrates can be accomodated. Protic solvents usually do not obey the relationships obtained for aprotic media and this appears to be due to the varying basicity of the substrates under consideration.

INTRODUCTION

About 100 years ago, chemists discovered that chemical reactions may be decisively influenced by the use of different solvents (1, 2). In 1920 BORN showed that the transfer of an ion from the gas to the solution phase is accompanied by a large decrease in free energy, i.e. a stabilization of the ion, which increases with increasing dielectric constant of the solvent (3). Several years later KIRKWOOD showed that in principle the same effect applies to molecules with a permanent dipole moment (4). Both theories have been widely used in various fields of chemistry and physical chemistry.
Based on an extensive body of experimental data nowadays available for non-aqueous solvents, it can be stated, that the purely elementary electrostatic approach in general does not provide a satisfactory interpretation of the observed solvent effects.
Attempts to describe substrate-solvent interactions by means of molecular electrostatic interaction models were essentially confined to the calculation of heats or free energies of hydration of monoatomic ions (5, 6). There appears to be little chance for the application of such models to non-aqueous solvents since too little is known about the charge distribution in the solvent and substrate molecules and the dynamics of the solvation process.
    Modern quantum mechanical methods are promising but until now too little data are available to satisfy the needs of the experimental chemist.
For this reason various chemists have tried to describe the influence of the solvent on chemical reactivity by means of empirical solvent parameters such as rate or equilibrium constants of certain standard reactions, electronic transition energies or IR frequencies of certain standard compounds etc., whose solvent dependence is considered as characteristic for the solvent influence on other chemical or physical processes (7). The crucial problem with the use of such parameters is, that the solvating power of a solvent is, in fact, a complex quantity, which depends on various factors such as solvent basicity, acidity, polarity, association of solvent molecules, the contributions of which may vary considerably with the substrate under consideration. It follows that a more general description of solvent effects should be possible only if parameters can be defined which allow a separate characterization of the various contributing factors (8).

SOLVATING POWER OF SOLVENTS

Short range substrate solvent interactions

Our present model is based on the view that direct interactions between substrate and solvent molecules may be considered as donor-acceptor interactions, the terms donor and acceptor being used in the widest sense of the word and not necessarily restricted to LEWIS acid-base type interactions. Depending on the nature of the substrate the solvent may act as donor or acceptor on use both functions at the same time (9). Donor and acceptor properties of solvents can be determined by means of suitably chosen reference compounds.

In 1966 GUTMANN and WYCHERA introduced as a measure of solvent basicity the socalled donor number, DN, defined as the negative ΔH-value for the 1 : 1 adduct formation between solvent molecules and the reference base $SbCl_5$ in 1,2-dichloroethane solution (10). Determination of an analogous quantity for the acceptor properties of solvents is not possible for principle reasons. In most cases, solvent molecules have closed electron shells and therefore do not form stoichiometric compounds even with strong reference bases. Recently we have shown that a suitable measure of solvent acceptor properties is provided by the solvent dependence of the ^{31}P NMR chemical shift of triethylphosphine oxide (11). This reference base contains a single basic center, namely the oxygen atom, whereas the acidic center of the molecule, the phosphorus atom is protected against nucleophilic solvent attack by the oxygen and the three largely inert alkyl groups. Electrophilic attack of the solvent molecules at the oxygen leads to a decrease in electron density at the phosphorus atom and a corresponding downfield shift which is considered proportional to the strength of the interaction. The acceptor number AN is defined by equ. (1) where δ_{corr} denotes the ^{31}P chemical shift of Et_3PO in some solvent S, extrapolated to zero concentration and refered to an infinitely dilute solution of the phosphine oxide in n-hexane, the denominator is the corresponding shift value for an infinitely dilute solution of the antimony pentachloride-triethylphosphine oxide adduct in 1,2-dichloroethane, whose acceptor number was arbitrarily assigned a value of 100, n-hexane has of course the acceptor number zero.

$$AN = \frac{\delta_{corr}}{\delta_{corr}(SbCl_5.Et_3PO)} \times 100 \tag{1}$$

Owing to the excellent solubility and stability of Et_3PO, acceptor numbers can be directly measured for all types of coordinating and non-coordinating solvents (11).

The influence of dielectric polarization of the solvent

By means of the donor and acceptor numbers it is possible to characterize short range substrate-solvent interactions. In case of ions or polar solutes there exist, in addition, long range interactions which result from the dielectric polarization of the solvent molecules. These latter contributions frequently constitute the main proportion of the total solvation energy.

Fig. 1 shows the standard free energies of transfer of K^+ for transfer from the reference solvent acetonitrile to various solvents S of medium to high dielectric constant as a function of the donor numbers (12). For aprotic solvents like NM, An, TMS, PDC, DMF and so forth there exists an excellent linear relationship suggesting that the observed trend is determined by the short range interactions, while the contribution from long range interactions appears to be essentially constant. From the known standard free energy of hydration of the potassium ion and by extrapolating the straight line to DN = zero, the free energy contribution resulting from dielectric polarization can be estimated as $\simeq$ - 75 kcal/grammion, compared with a change in the short range interaction energies of only 9 kcal/grammion for the solvents investigated (8). In other words, in solvents of medium to high dielectric constant, the changes in chemical reactivity of the potassium ion on solvent transfer are determined by the short range interaction energies although the latter amount to only several percent of the total solvation energy.
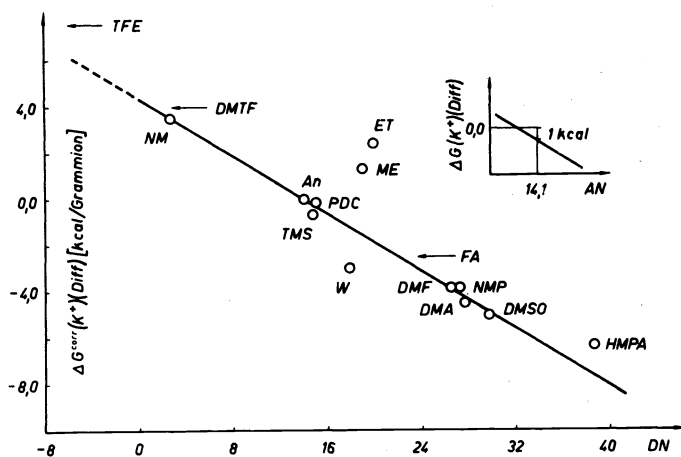
Fig. 1. Standard free energies of transfer of the potassium ion for transfer from acetonitrile to various solvents as a function of their donor numbers.

A similar situation was found for the halide ions. Fig. 2 shows the relationship between the standard free energies of transfer of the chloride ion for transfer from acetonitrile to various solvents as a function of their acceptor numbers (12). For aprotic solvents of medium to high dielectric constant there exists an excellent linear relationship with a change in ΔG of only about 5 kcal/grammion for transfer from HMPA to DMSO which differ by about 10 acceptor number units. The total free energy change for transfer of the chloride ion from the gas phase into these solvents is in the order of about - 65 kcal/grammion (8). This shows, that the changes in chemical reactivity of the chloride ion in high dielectric constant solvents are again mainly a function of the short range interactions.
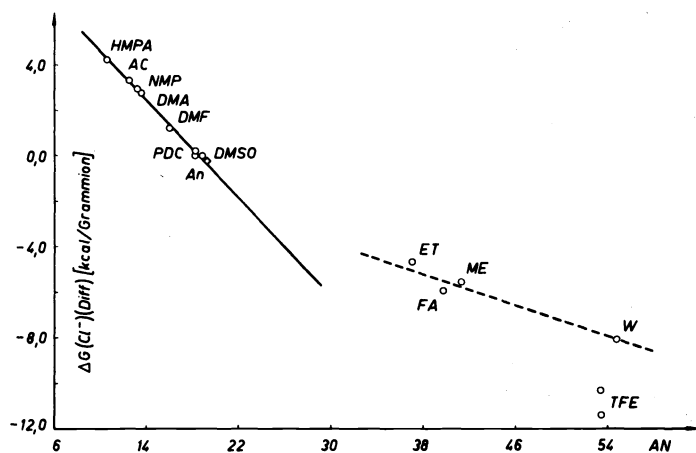

Fig. 2. Standard free energies of transfer of the chloride ion for transfer from acetonitrile to various solvents as a function of their acceptor numbers.

Protic solvents show positive deviations from the linear relationship i.e. the chloride icn is less strongly solvated by protic solvents than one would expect from their acceptor numbers and this is typical for many other chemical and physical processes as we shall see later. One possible reason for this behaviour might be different contributions from hydrogen bonding to the total short range interaction energy. Triethylphosphine oxide is a very strong base with a donor number of > 40, so that hydrogen bonding probably constitutes the main contribution to the total short range interaction energy. Substrates which are much weaker donors than Et_3PO will therefore be less strongly solvated by protic solvents. This interpretation agrees with the observation that the solvating ability of protic relative to aprotic solvents decreases in the order Cl^-, Br^-, I^-, i.e. with decreasing donor strength of the ions. For example, towards the chloride ion, protic solvents are generally better solvators than aprotic media (Fig. 2),whereas towards the iodide ion (Fig. 3), aprotic solvents like PDC, An or DMSO show about the same solvating ability as protic solvents.
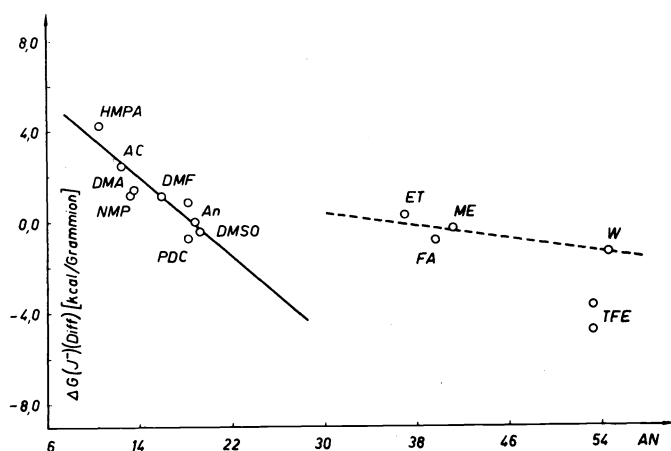

Fig. 3. Standard free energies of transfer of the iodide ion for transfer from acetonitrile to various solvents as a function of their acceptor numbers.

A second factor which might also contribute to the irregular behaviour of protic solvents, are profound changes in solvent structure caused by the solute on transfer of the solute from the gas phase into the solvent. Acceptor numbers reflect the final state of solvation in solution and are therefore not expected to allow for energy contributions due to a reorientation of associated solvent molecules in course of the solvation process.

Energy of cavity formation

When a substrate is transferred from the gas phase into a solvent, one should expect that it is first necessary to make a hole in the solvent in which the substrate can be accommodated.

Many efforts have been made to evaluate the energy contribution of hole formation to the total solvation energy (13 - 15). The present approach is based on the assumption that the free energy of cavity formation for a given substrate is related to the free energy change required to create cavities in a liquid, the size of which corresponds to the volume occupied by the respective solvent molecules (8). The latter quantity has been shown to be related to the standard free energy of vaporization of the solvent (8).

Whereas the problem of cavity formation is of principal theoretical interest, it frequently turns out in practice that the influence on changes in chemical reactivity of a given system on solvent transfer, is usually small or even negligible (16). In many cases this appears to be due to the fact, that the corresponding free energy terms for reactants and products are largely compensating each other.

Using appropriate thermochemical cycles and taking into account the various contributions to the free energy of solvation of a substrate, mentioned before, the influence of the solvent on chemical reactivity can be represented by equ. (2)

$$\underbrace{\Delta G^S - \Delta G^R}_{\Delta\Delta G} = a.\underbrace{(DN^S - DN^R)}_{\Delta DN} + b.\underbrace{(AN^S - AN^R)}_{\Delta AN} + c.\underbrace{(\Delta G_{vp}^{oS} - \Delta G_{vp}^{oR})}_{\Delta G_{vp}^o} \qquad (2)$$

where ΔG^S and ΔG^R denote the standard free energies of reaction or activation of a given process in various solvents S and a fixed reference solvent R, and where DN, AN and ΔG_{vp}^o are the corresponding donor numbers, acceptor numbers and standard free energies of vaporization (8). This equation was originally applied to non-associated solvents of medium to high dielectric constant where the free energy contribution from dielectric polarization may be assumed to be essentially constant (16).
Donor and acceptor numbers for various solvents are listed in Table 1. Values ΔG_{vp}^o have been published elsewhere (16, 17).

TABLE 1.   Donor and acceptor numbers for various solvents

Solvent	DN	AN	Solvent	DN	AN
Hexane	0,0	0,0	Water	18,0	54,8
Carbon tetrachloride	0,0	8,6	Phenylphosphonic		
1,2-Dichloroethane (DCE)	0,0	16,7	dichloride	18,5	--
Sulfuryl chloride	0,1	--	Methanol	19,0	41,3
Benzene	0,1	8,2	Ethanol	--	37,1
Thionyl chloride	0,4	--	Trifluoroethanol	--	53,3
Acetyl chloride	0,7	--	iso-Propanol	--	33,5
Tetrachloroethylene			Ethylene glycol dimethyl		
carbonate	0,8	--	ether (glyme)	--	10,2
Dichloromethane	--	20,4	Diethylene glycol dimethyl		
Chloroform	--	23,1	ether (diglyme)	--	9,9
Benzoyl fluoride	2,0	--	Dioxane	--	10,8
Benzoyl chloride	2,3	--	Diethyl ether	19,2	3,9
Nitromethane (NM)	2,7	20,5	Tetrahydrofuran (THF)	20,0	8,0
Dichloroethylene			Formamide	--	39,8
carbonate	3,2	--	Diphenylphosphonic		
Nitrobenzene (NB)	4,4	14,8	chloride	22,4	--
Acetic anhydride	10,5	--	Trimethyl phosphate (TMP)	23,0	16,3
Phosphorus oxychloride	11,7	--	Tributyl phosphate (TBP)	23,7	9,9
Benzonitrile (BN)	11,9	15,5	N-Methylformamide (NMF)	--	32,1
Selenium oxychloride	12,2	--	N,N-Dimethylforma-		
Acetonitrile (An)	14,1	18,9	mide (DMF)	26,6	16,0
Sulfolane (TMS)	14,8	19,2	N,N-Dimethylthioforma-		
Propanediol-1,2-carbo-			mide (DMTF)	--	18,8
nate (PDC)	15,1	18,3	N-Methyl-ε-caprolactame	27,1	--
Benzyl cyanide	15,1	--	N-Methyl-2-pyrrolidinone		
Ethylene sulphite	15,3	--	(NMP)	27,3	13,3
iso-Butyronitrile	15,4	--	N-Methyl-2-thiopyrrolidi-		
Propionitrile	16,1	--	none	--	17,7
Ethylene carbonate	16,4	--	N,N-Dimethylacetamide		
Phenylphosphonic			(DMA)	27,8	13,6
difluoride	16,4	--	Dimethyl sulphoxide (DMSO)	29,8	19,3
Methylacetate	16,5	10,7	N,N-Diethylformamide	30,9	--

TABLE 1. (continued)

Solvent	DN	AN	Solvent	DN	AN
n-Butyronitrile	16,6	--	N,N-Diethylacetamide	32,2	--
Acetone (AC)	17,0	12,5	Pyridine (Py)	33,1	14,2
Ethyl acetate	17,1	9,3	Hexamethylphosphorictri-		
			amide (HMPA)	38,8	10,6
			Ethanolamine	--	33,7
			Ethylenediamine	--	20,9
			Morpholine	--	17,5
			Diethylamine	--	9,4
			Triethylamine	61,0	1,4
			Acetic acid	--	52,9
			Formic acid	--	83,6
			Trifluoroacetic acid	--	105,3
			Methanesulfonic acid	--	126,3
			Trifluoromethane-		
			sulfonic acid	--	129,1

We shall now demonstrate the scope and limitations of our model for various chemical and physical processes.

SELECTED EXAMPLES FOR THE SOLVENT INFLUENCE ON CHEMICAL AND PHYSICAL PROCESSES

Inorganic systems

TABLE 2.   Standard free energies of solution (kcal/mole) of NaCl in various solvents at 25 C. Data are from reference (16).

Solvent	ΔG(exp.)	ΔG(calc.)	
		equ. (3)	equ. (4)
formamide	- 0,09	(- 2,49)	(- 2,44)
N-methylformamide	0,90	(- 0,04)	(0,06)
methanol	3,37	(- 0,87)	(- 1,32)
dimethylsulfoxide	3,57	3,51	3,53
dimethylformamide	6,41	6,53	6,44
dimethylacetamide	7,02	6,98	6,96
N-methylpyrrolidone	7,25	7,25	7,32
sulfolane	10,01	10,16	10,37
propylenecarbonate	10,69	10,53	10,67
acetonitrile	11,18	11,17	10,86

$$\Delta\Delta G = -0,457.\,\Delta DN - 0,436.\,\Delta AN - 0,102.\,\Delta\Delta G_{vp}^{o} - 0,008$$
$$R = 0,999, \quad \sigma = 0,08. \tag{3}$$

$$\Delta\Delta G = -0,456.\,\Delta DN - 0,442.\,\Delta AN - 0,323$$
$$R = 0,997, \quad \sigma = 0,13 \tag{4}$$

Table 2 shows the solvent influence on the solubility of NaCl in various solvents. Column 2 lists the experimental standard free energies of solution, calculated from the solubility products, columns 3 and 4 values calculated by our equation using first all three parameters (equ. (3)) and then only the parameters DN and AN (equ. (4)). Comparison of the two equations shows, that the regression coefficients for DN and AN as well as the correlation coefficients R are very similar, indicating that the influence of the cavity term is small. This may be attributed to the small volume requirement of the ions under consideration. The mean deviation σ between experimental and calculated values is 0,08 and 0,13 kcal, respectively, which is extremely good in view of the fact that the spread in ΔG values for aprotic solvents corresponds to a difference in solubility products of nearly six powers of ten. Calculated values for protic solvents (given in parenthesis) are considerably more negative than the experimental ones which corresponds exactly to the irregular behaviour observed for the transfer energies of the chloride ion (Fig. 2).

From the regression equations it is clear that the solubilities depend both on the donor and acceptor properties of the solvents and this is the reason why various other classical solvent parameters such as Z, E_{T}, G or δ -values or the dielectric constant fail to reproduce the observed solvent influence.

Attention should be paid to the coefficients of the regression equations which give information about the donor and acceptor properties of the solutes. The donor number coefficient 0,46 for example indicates that the acceptor strength of the Na^{+} ion is about one half of that of $SbCl_5$. The acceptor number coefficient 0,44 agrees fairly satisfactorily with the value 0,54 derived from the free energy of transfer-acceptor number plot of the chloride ion shown before.

TABLE 3.   Standard free energies of solution (kcal/mole) of KCl in
            various solvents at 25 C. Data are from reference (16)

Solvent	ΔG(exp.)	ΔG(calc.)
formamide	0,56	(- 2,76)
N-methylformamide	1,65	(0,24)
methanol	4,35	(- 2,28)
dimethylsulfoxide	4,70	4,77
dimethylformamide	7,49	7,28
dimethylacetamide	7,94	8,04
propylenecarbonate	9,44	9,67
acetonitrile	9,88	9,70

$$\Delta\Delta G = - 0,302.\Delta DN - 0,467.\Delta AN - 0.186$$
$$R = 0,996, \quad \sigma = 0,16. \tag{5}$$

Similar results were obtained for KCl, Table 3. Omission of the cavity term gives equ. (5) with an excellent correlation coefficient R = 0,996 and δ = 0,16 indicating excellent agreement between experimental and calculated values. The influence of the donor properties is somewhat weaker than in case of NaCl as reflected by the smaller donor number coefficient 0,30 which is a measure of the acceptor properties of the potassium ion and which agrees perfectly with a value of 0,31 obtained independently from emf measurements (12).

Calculated solubilities for protic solvents are again much higher than the experimental values.

By means of such equations solubilities of electrolytes may be predicted for many other high dielectric constant solvents, provided their donor and acceptor numbers are known.

TABLE 4.   Standard free energies (kcal/mole) for the reaction
            $CoCl_3^- + Cl^- \longrightarrow CoCl_4^{2-}$ in various solvents
            at 25 C. Data are from reference (16)

Solvent	ΔG(exp.)	ΔG(calc.)
nitromethane	- 6,59	- 6,42
acetone	- 4,69	- 4,69
acetonitrile	- 3,92	- 4,13
dimethylacetamide	- 2,05	- 2,02
dimethylformamide	- 1,64	- 1,83
dimethylsulfoxide	- 0,59	- 0,47
hexamethylphosphorictriamide	- 0,16	- 0,08

$$\Delta\Delta G = 0,228 . \Delta DN + 0,191 . \Delta AN - 0,209$$

$$R = 0,998, \delta = 0,11. \tag{6}$$

Table 4 shows the solvent influence on the formation of the $CoCl_4^{2-}$ complex from $CoCl_3^-$ and Cl^-. The experimental standard free energies of formation can be reproduced by means of the parameters DN and AN with a mean deviation δ of only 0,11 kcal/mole. The influence of the donor number is due to the fact, that the trichlorocobaltate ion is tetrahedrally coordinated with a solvent molecule as fourth ligand. With increasing donor number this complex becomes more stable so that the equilibrium should be shifted to the left hand side as evidenced by the positive sign of the donor number coefficient. The acceptor number coefficient is composed of the individual coefficients of the anions. From the fact, that a chloride ligand in the $CoCl_4^{2-}$ ion is certainly less effectively solvated than a free chloride ion, it follows that the <u>electrophilic</u> action of the solvent should cause a shift in equilibrium to the left hand side with increasing acceptor numbers. As expected the acceptor number coefficient is indeed positive and lower than the corresponding coefficient for the free chloride ion (0,54). The value of the donor number coefficient (0,23) indicates that the acceptor strength of the hypothetical, unsolvated $CoCl_3^-$ ion is only one fourth of that of antimony pentachloride.

Kinetics of organic reactions

According to Eyrings theory of absolute rates there exists an equilibrium between reactants or products and their corresponding transition states. Application of our model to such equilibria allows the calculation of free energies of activation and rate constants, respectively, and this shall be demonstrated by a few examples.

Fig. 4 shows the solvent dependence of the first order rate constants for the solvolysis of t-butyl chloride. This classical reaction was first systematically investigated by WINSTEIN and coworkers who proposed the logarithm of the rate constant relative to that in 80 % aqueous ethanol as a measure of "solvent ionizing power", known as Y-value (19).
    For aprotic solvents there exists a good linear relationship with the acceptor numbers, which has to be ascribed to the solvation of the developing chloride ion in the polar transition state complex. It has been frequently stated that solvolysis of tertiary alkyl halides proceeds without nucleophilic solvent assistence. Regression analysis for aprotic solvent gives equ. (7) which indicates a small but significant contribution from the donor properties of the solvents and which may be ascribed either to interactions with the carbonium carbon or with the positivated hydrogen atoms of the transition state complex (20).

$$\Delta\Delta G^{\ddagger} = - 0,065 . \Delta DN - 0,421 . \Delta AN - 0,719$$
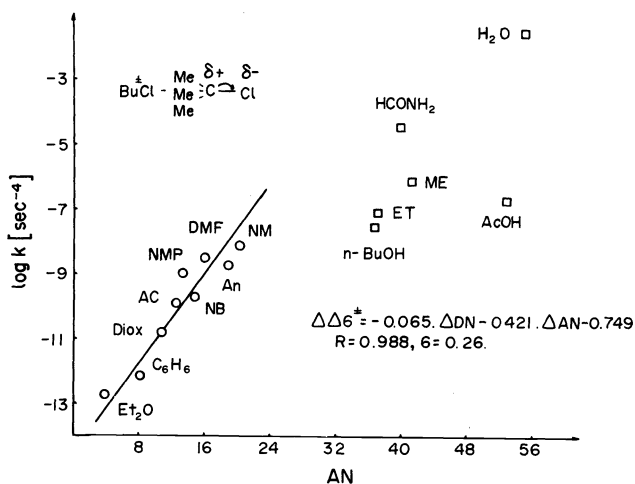
$$R = 0,988, \delta = 0,26 \tag{7}$$

Fig. 4.   Relationship between solvent acceptor numbers and rates of
          solvolysis of t-butyl chloride. Rate constants are from ref. (18).

Inclusion of the cavity term does not significantly improve the correlation. As expected for
a partially ionized C—Cl bond, the acceptor number coefficient is smaller than the
corresponding coefficient for the free chloride ion (0, 54). Both coefficients are negative,
i. e. the reaction is accelerated with increasing donor and acceptor numbers.
It is noteworthy that the correlation also includes solvents with low dielectric constants
such as diethyl ether, benzene and dioxane, suggesting that acceptor numbers might
possibly include contributions from long range dipolar interactions.
Rates in protic solvents like water, methanol, ethanol, formamide etc. are much smaller
than expected from their acceptor numbers. As already mentioned this may be explained
by the assumption, that the negativated chlorine atom in the transition state complex is
most probably a weaker donor than Et_3PO, so that hydrogen bonding makes a weaker
contribution to the solvating power than in case of the strong reference base Et_3PO. This
is further substantiated by the observation that the reaction in acetic acid is much slower
than in water although these solvents have nearly the same acceptor numbers. Liquid
acetic acid is known to consist mainly of cyclic dimers which are sufficiently stable to
persist even in the gas phase. Consequently, acetic acid will display its potentially high
acidity towards bases only, which are sufficiently strong to break up the dimers, whereas
it will behave as a comparatively poor acceptor solvent towards weakly basic substrates.
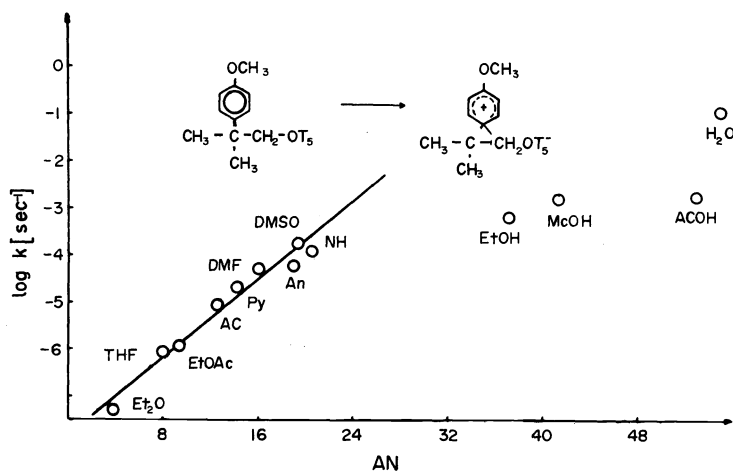

Fig. 5.   Relationship between solvent acceptor numbers and rates of solvolysis
          of p-methoxyneophyl toluenesulfonate. Rate constants are from
          ref. (21).

Fig. 5 shows another classical S_N1 reaction, namely the solvolysis of p-methoxyneophyl toluenesulfonate. Logarithms of the rate constants in aprotic solvents are linearly related to the acceptor numbers whereas rates in protic solvents, as in case of t-butyl chloride, are much slower than expected from their acceptor numbers. A multiple linear regression analysis confirms, that this anchimerically assisted reaction depends only on the acceptor numbers without any noticeable influence from the solvent donor properties and thus obviously represents the special case of a socalled "limiting solvolysis reaction".
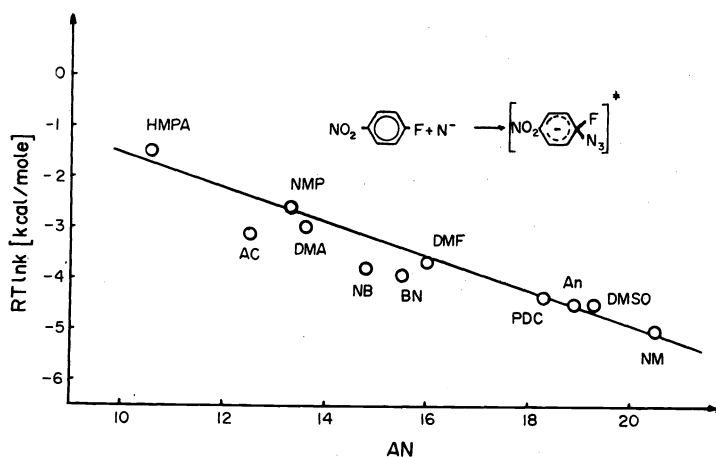
Fig. 6.   Relationship between solvent acceptor numbers and second
          order rate constants for the substitution of fluorine in
          p-nitrofluorobenzene by azide ion. Data ate from ref. (16).

Fig. 6 shows the solvent influence on a bimolecular nucleophilic aromatic substitution reaction, namely the substitution of fluorine in p-nitrofluorobenzene by azide ion. Logarithms of the rate constants decrease with increasing acceptor numbers of the solvents. This is explained by the fact that the transition state anion is less basic than the azide ion so that the reactants become more stable relative to the transition state complex with increasing acceptor properties of the solvents. The small deviations from the straight line observed for acetone, nitrobenzene and benzonitrile are due to ion-pairing of NEt_4N_3 used as source of the azide ions. Corrected rate constants are close to the straight line.
In protic solvents like water, methanol or formamide, the reaction proceeds even slower than in aprotic solvents, but definitely faster than expected from the straight line (16) in perfect agreement with the behaviour found in the systems discussed so far. The azide ion, being a weaker base than Et_3PO, is less effectively stabilized in protic solvents which corresponds to a relative decrease in free energy of activation or relative increase in rate, respectively. The results of a multiple linear regression analysis confirm, that the reaction depends almost exclusively on the acceptor properties of the solvents, equ. (8).

$$\Delta\Delta G^{\neq} = 0,339 . \Delta AN + 0,024$$

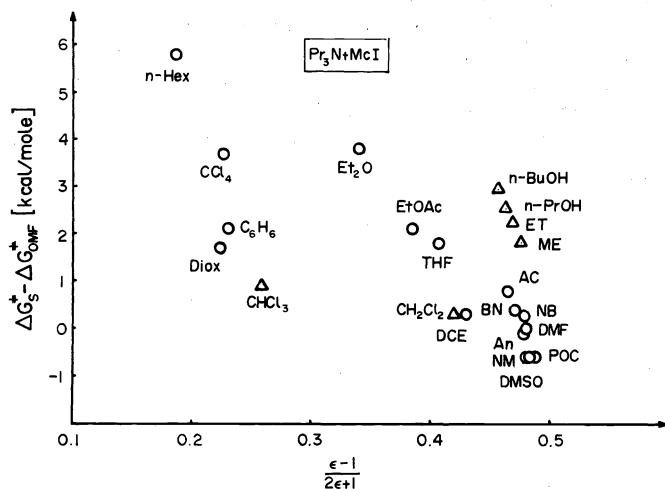$$R = 0,992, \quad \delta = 0,11. \tag{8}$$

Fig. 7. Relationship between KIRKWOOD function and standard free
         energies of activation for the reaction of tripropylamine with
         methyl iodide refered to the reference solvent DMF.   ΔG-values
         are from refs. (23) and (24).

Anorther important group of bimolecular nucleophilic substitution reactions are the
MENSCHUTKIN   reactions. As an example we consider the reaction between tripropyl-
amine and methyl iodide which has been studied in a wide range of solvents (22).   In this
reaction, as in all other MENSCHUTKIN reactions,   neutral molecules react to a
polar transition state, so that this type of reaction should be particularly suited for the
application of the KIRKWOOD theory.
The results are shown in Fig. 7 where the standard free energies of activation, refered
to the solvent DMF are plotted versus the KIRKWOOD function. The correlation is very
poor, demonstrating the failure of the purely elementary electrostatic approach.
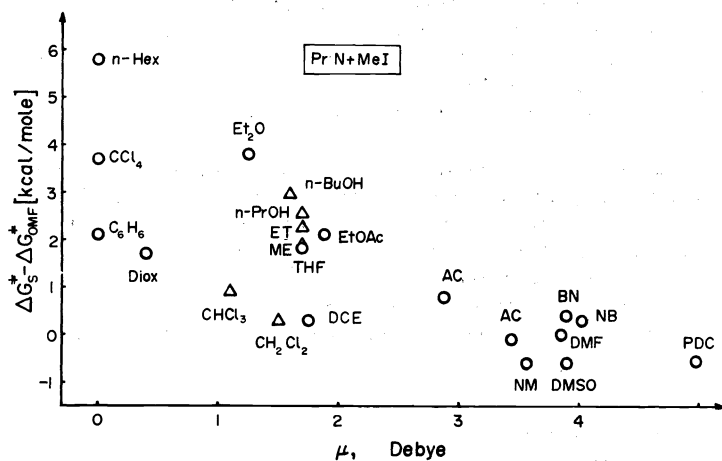

Fig. 8. Relationship between solvent dipole moments and standard free
         energies of activation for the reaction of tripropylamine with
         methyl iodide refered to the reference solvent DMF. ΔG-values
         are from refs. (23) and (24).

A similarly poor correlation is obtained if the activation energies are plotted versus the dipole moments of the solvent molecules, Fig. 8.
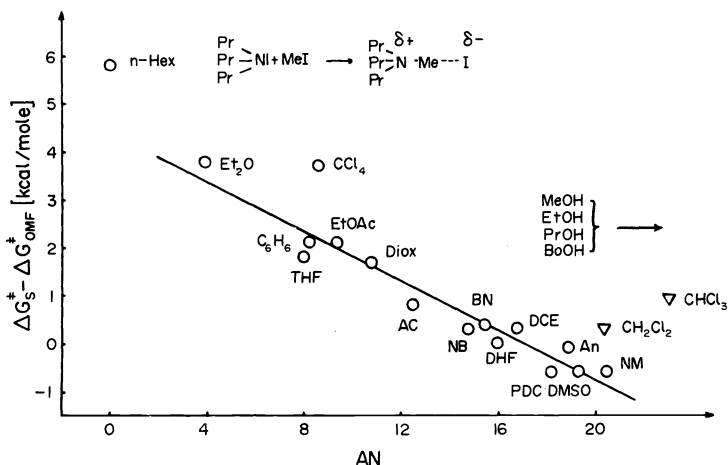

Fig. 9.   Relationship between solvent acceptor numbers and standard
          free energies of activation for the reaction of tripropylamine
          with methyl iodide refered to the reference solvent DMF.
          Δ_iG values are from refs. (23) and (24).

In contrast, the standard free energies of activation correlate quite well with the acceptor numbers Fig. 9. Out of 16 aprotic solvents only two, namely CCl_4 and Et_2O are off line. As expected the rates increase with increasing acceptor numbers owing to the solvation of the developing iodide ion in the polar transition state complex. The slope of the straight line, approximately 0,26 kcal/per acceptor number unit is consistent with a value of 0,43 found for the free iodide ion from recent emf measurements (12).
Protic solvents like dichloromethane, chloroform and the alcohols show the now already familiar positive deviations from the acceptor number plot which, in the present case, might also partly arise from specific hydrogen bond interactions with the tertiary amine.

     Some authors like FOWLER and KATRIZTKY (25) or KOPPEL and PALM (26) have tried to improve correlations with empirical solvent parameters by including dielectric constant functions. In case of the present reaction, inclusion of a KIRKWOOD function term does not significantly improve the correlation and the same is true for the donor number and cavity term. The absence of a donor influence indicates that the hydrogen atoms of the transition state complex are not sufficiently acidic to undergo charge transfer interactions with bases.
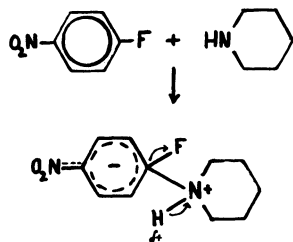

Fig. 10.

A quaternization reaction which is influenced both by the acceptor and donor properties of the solvent is the bimolecular reaction between p-nitrofluorobenzene and piperidine, Fig. 10. Addition of piperidine enhances the acidity of the NH-hydrogen atom and the basicity of the p-nitrofluorobenzene group, so that the transition state complex is solvated both by nucleophilic and electrophilic solvent attack. A multiple linear regression analysis for twelve low to high dielectric constant solvents gives equ. (9).

$$\Delta\Delta G^{\neq} = -0,101.\Delta DN - 0,247.\Delta AN - 0,384$$
$$R = 0,976, \quad \delta = 0,27 \tag{9}$$

The values R and δ indicate good agreement between calculated and experimental data which cover a range in rate constants of about 10^4 (Table 5). The donor number coefficient 0,10 may be considered as a measure of the acidity of the NH-hydrogen in the transition state complex and agrees well with values recently obtained for the acceptor properties of the NH-hydrogens in tertiary ammonium ions (16).
Similar to the tripropylamine reaction experimental rates in protic solvents are by several powers of ten lower than the calculated ones.

TABLE 5.   Rate constants ($1.\text{mole}^{-1}.\text{sec}^{-1}$) for the reaction of
p-nitrofluorobenzene with piperidine in various solvents
at 25 C. Data are from reference (27)

Solvent	RTln $k_{exp.}$	RTln $k_{calc.}$
benzene	- 7,39	- 7,69
ethyl acetate	- 5,96	- 5,69
dimethoxyethane	- 5,84	- 5,37
methyl acetate	- 5,71	- 5,41
tetrahydrofuran	- 5,67	- 5,72
acetone	- 4,69	- 4,91
benzonitrile	- 4,68	- 4,69
nitromethane	- 4,21	- 4,38
acetonitrile	- 4,01	- 3,63
dimethylformamide	- 2,91	- 3,08
dimethylacetamide	- 2,85	- 3,55
dimethylsulfoxide	- 2,13	- 1,94
i-propanol	- 5,28	(0,52)
methanol	- 5,25	(2,41)
ethanol	- 5,25	(1,41)

Spectroscopic properties
Besides equilibrium and rate data, our solvent parameters may be successfully applied to represent the solvent influence on various spectroscopic properties.
Fig. 11 shows as an example the solvent influence on the ^{13}C NMR chemical shift of the carbonyl carbon of acetone. As you see, we have originally drawn a common straight line for aprotic and hydroxylic solvents but in the light of our present knowledge it appears more likely that different lines would emerge if the correlation would be extended to a wider range of solvents.
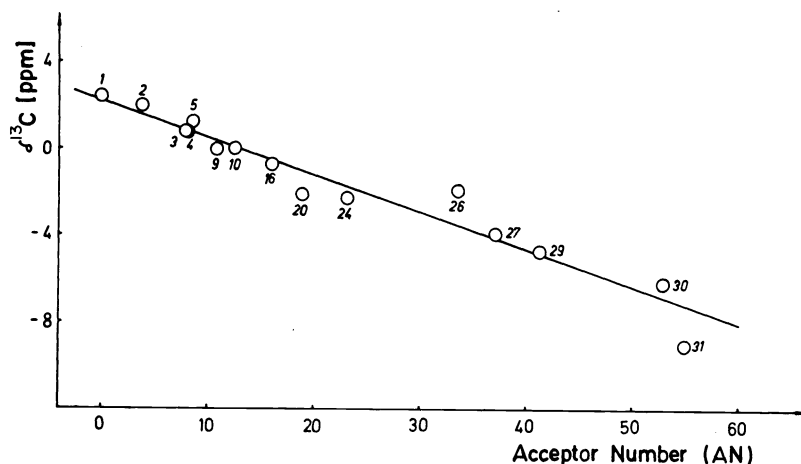
Fig. 11.   Relationship between solvent acceptor numbers and the $^{13}C{=}O$ NMR chemical shift of acetone. Data are from ref. (11).
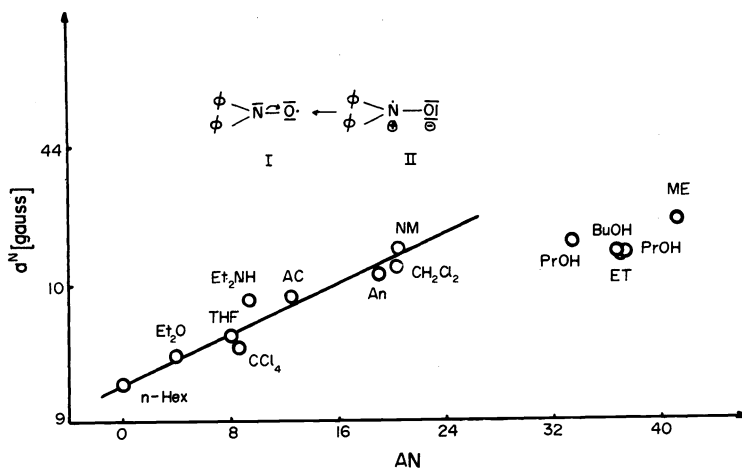

Fig. 12.   Relationship between solvent acceptor numbers and the ESR nitrogen coupling constant of the diphenyl nitroxide radical. Coupling constants are from ref. (28).

Fig. 12 shows the solvent influence on the ESR nitrogen coupling constant of the diphenyl nitroxide radical. The observed increase in the coupling constant with increasing acceptor numbers is due to electrophilic solvent attack at the oxygen atom which leads to an increasing stabilization of the mesomeric structure II and hence to an increase in spin density at the nitrogen atom. Coupling constants in hydroxylic solvents are again somewhat lower than expected from their acceptor numbers.
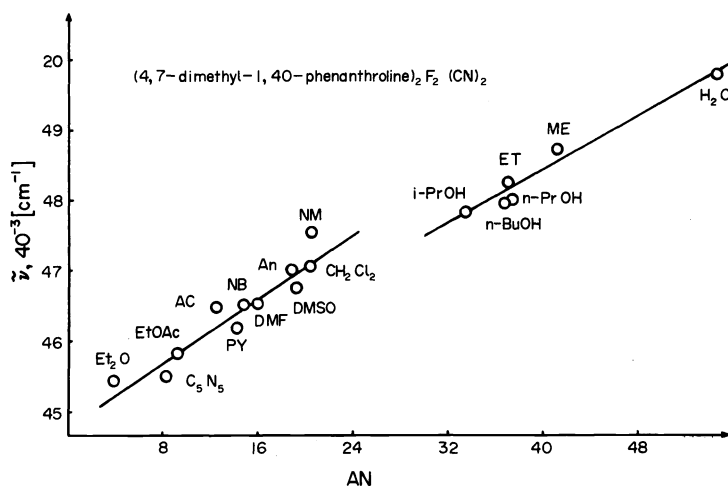
Fig. 13. Relationship between solvent acceptor numbers and wave-
numbers for the low energy electronic absorption band of
(4, 7 - dimethyl - 1, 10 - phenanthroline)$_2$Fe(CN)$_2$. Wavenumbers
are from ref. (29).

Fig. 13 shows as the final example the solvent influence on the highest wavelength
electronic absorption band of a Fe(II)-dicyanophenanthroline complex. Wavenumbers of
this band, which has been assigned to metal to ligand charge transfer, increase with
increasing acceptor numbers indicating that solvent attack occurs electrophilically at the
cyanide ligands. Wavenumbers for protic solvents lie on a separate line and are lower
than expected from the acceptor numbers, suggesting that the complex is a weaker base
than Et$_3$PO.
Correlations of this type may give valuable informations about the mechanism of the charge
transfer process. The observed positive slope of the straight line is consistent with a
metal to phenanthroline ligand charge transfer whereas a negative slope would be
expected for a ligand to metal transition.
As in case of the tripropylamine reaction, poor correlations are obtained if the
wavenumbers are plotted versus the dipole moments or the KIRKWOOD function.

SUMMARY AND CONCLUSION

In summary it appears at the present state of theory, that solvent effects on chemical or
physical processes may be described best at least for the needs of the experimental chemist
by means of carefully selected empirical solvent parameters. A basic requirement for
a fairly general description of solvent effects is the use of model substrates which allow
a separate characterization of nucleophilic and electrophilic solvent properties. Various
classical empirical solvent parameters, such as the Z, E$_T$ or Y-values, which in part
have been quite successfully used in the study of solvent effects, do not represent a
general measure of solvent polarity or solvent ionizing power but are obviously closely
related to the solvent acceptor properties.
In order to avoid confusion we suggest that the term solvent polarity should be used only for
the dipolar properties of the solvent molecules, whereas the ionizing or solvating power
of a solvent, as already mentioned, stems from different factors whose relative
contributions may vary considerably with the substrate under consideration.
We further wish to emphasize the special behaviour of hydrogen bonding solvents. The
acceptor properties of these solvents relative to aprotic solvents may vary considerably
with the basicity of the solute owing to the different contributions of hydrogen bonding to
the total interaction energy.

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