Coordination Chemistry Reviews, 43 (1982) 133–164
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

STRUCTURAL VARIABILITY IN SOLUTIONS

VIKTOR GUTMANN, GERHARD RESCH and WOLFGANG LINERT

Institut für Anorganische Chemie, Technische Universität Wien, Getreidemarkt 9, 1060 Vienna (Austria)

CONTENTS

A. INTRODUCTION

The properties of a given molecular species may be varied by changing its molecular environment. Within a given solvent its properties may be varied by changes in concentration, temperature, pressure, by addition of other solutes and possibly even by the action of mechanical forces, which appears, however, not to have been investigated.

According to the quantum-chemical approach, a given molecular system is represented by its charge density pattern. The relative mean positions of the atomic nuclei are expressed by bond angles and bond lengths (internuclear distances). Chemical changes are ascribed to changes in electron densities; changes in internuclear distances (and bond angles) connected with them, are usually not given proper attention.

Interactions between molecular units lead to new systems, the properties of which cannot be accounted for from the properties of the interacting species alone [1].

The extended donor–acceptor approach provides a qualitative formulation of quantum-chemical conclusions in terms familiar to the chemist. Simple rules are provided for the changes in internuclear distances resulting from interactions [2]. They provide information on the statistical aspects of the structural variations. These will be considered from various points of view in sections B and C.

The statistical approach, however, does not account for the differentiation of the parts in microscopic regions. Variations of the parts take place continuously due to their interdependent and interrelated motions. The particle model alone cannot account fully for the dynamic system properties. The authors therefore take into consideration the continuum aspects of matter, as they are implied in the quantum-chemical model [1].

B. STRUCTURAL VARIATIONS DUE TO INTERACTIONS BETWEEN TWO MOLECULES AS BASED ON STATISTICAL RESULTS

(i) The donor–acceptor approach

The donor–acceptor approach is based on qualitative observations. Measurable quantities as such are not considered but they are related to quantities found for the system under different conditions, especially different molecular environments. Structural changes of a given molecular species due to changes in environment are related to measured differences in thermodynamic, spectroscopic, or kinetic properties. Such relations are independent from the interpretation of binding forces; the concept may be applied almost universally to any kind of molecular interaction [2]. The donor–acceptor concept provides an understanding of changes in properties due to interactions. It is therefore more flexible and in better agreement with reality than the models which are based on idealizations.

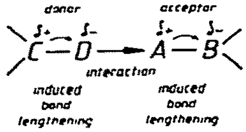
Simple rules have been provided, namely the so-called "bond length variation rules", the "pileup effect at the donor atom", and the "spillover effect at the acceptor atom" [2], which have recently been referred to as "Gutmann rules" [3].

An interaction between two molecular species is described by considering one of them as the electron donor and the other one as the electron acceptor [1–4]. The electron donor with its region of high electron density interacts with the area of low electron density of the electron acceptor. The result is a new system in which border lines between the two original species cannot be drawn unambiguously [1].

(ii) The first bond length variation rule

Experience shows that the bonds originating from the donor atom D in the donor component and those originating from the acceptor atom A in the acceptor component are lengthened [2,4].

The increase in internuclear distances may be indicated by a full bent arrow above the two atomic symbols, which points in the direction of the charge transfer. The intramolecular bond lengthening induced by the intermolecular interaction is greater the stronger the latter and hence within a homologous series greater the shorter the intermolecular bond. For example the B–F bonds are longer in adducts of BF_3 than in the isolated gaseous molecule [2]. They are longer in the adduct $(CH_3)_3N \cdot BF_3$ than in $H_3N \cdot BF_3$, where the intermolecular B–N bond is longer than in the former. This is related to the stronger donor properties of $(CH_3)_3N$ compared to those of NH_3. An inverse relationship between intermolecular and adjacent intramolecular bond distances has been found in many other cases [2]. For example, in crystalline D_2CuX_2 complexes the equatorial bonds may be considered as intramolecular and the axial bonds, completing distorted octahedra, as intermolecular. Indeed, the equatorial bonds are lengthened as the axial bonds are shortened [5].



Intramolecular bond lengthening is found to occur when an electon shift occurs from the less electronegative to the more electronegative atom. This condition applies usually to the bonds adjacent to the sites of an intermolecular donor–acceptor interaction. Bond lengthening involves increase in bond polarity [6], i.e. increase in negative net charge at the more electronegative atom and increase in positive net charge at the less electronegative atom.

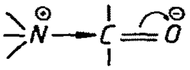
(iii) Pileup and spillover effects as required by the first bond length variation rule

As bond lengthening is associated with increase in bond polarity [6], both the negative net charge at D and the positive net charge at A are increased. This might not be expected, as in the course of the donor–acceptor interaction negative charge is transferred from D of the donor molecule toward A of the acceptor molecule. However, the original loss of negative charge at the donor atom D is overcompensated by the induced transfer of negative charge from other parts of the donor molecule toward the donor atom. This phenomenon has been named "pileup effect" of negative charge at the donor atom [1,7].

By analogy, the original gain of negative charge by the acceptor atom A of the acceptor component is passed on to other parts of the latter, including part of the electron density which originally resided at the acceptor atom A in the free acceptor component. The resulting increase in positive net charge at A is known as the "spillover effect" of negative charge at A [1,7].

The charge density redistribution as initiated by charge transfer from the donor component to the acceptor component results in increasing positive net charges of the more electropositive atoms, for example the hydrogen atoms in $H_3N \cdot BF_3$, as well as in increasing negative net charges of the more electronegative atoms, i.e. the fluorine atoms in the said compound. The increased polarization is reflected in increased reactivities; in the authors' example the acceptor properties of the (external) hydrogen atoms and the donor properties of the (external) fluorine atoms are enhanced [4].

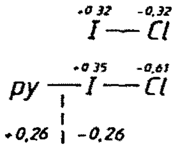
The representation of the charge redistribution as used in organic chemistry denotes the charge transfer between the component molecules and not the changes in net charge at the donor atom; the positive charge assigned to the N atom after nucleophilic attack, as expressed by



is not in agreement with the facts [2].

Experimental evidence for the pileup and the spillover effect has been provided by the results of NQR spectrometry for the complexes of 3,5-dibromopyridine with ICl, IBr and Br_2 [8] and by Mössbauer measurements [9] for the system pyridine–iodine.

The spillover effect at the hydrogen atoms of acetamide has been mea-



sured in different solvents by the NMR chemical shift [10] and at the antimony atom of adducts of antimony pentachloride in quick-frozen solutions by the ESCA technique [11].

As bond lengthening may be considered as an intermediate step in the course of heterolysis, pileup and spillover effects are "building up" the charges for the ions and hence they are a requirement for the process of ionization in solution [2].

These effects have also been shown to occur at phase boundaries, for example at a solid–gas interface: the adsorption of donor molecules at an aerosile surface leads to an increase in O–H-bond lengths at the surface, as the D → H bond is formed [12]. Hence the positive net charges at the hydrogen atoms are increased and so are the negative net charges at the donor atoms of the adsorbed molecules.

Thus, an electric double layer is formed even at a solid–gas interface. The electric double layer provides for the state of tension, which is necessary for the co-existence of the contacting phases. An analogous interpretation of the electric double layer at solid–liquid phase boundaries will be given elsewhere [13].

(iv) Pileup and spillover effects resulting from quantum-chemical calculations

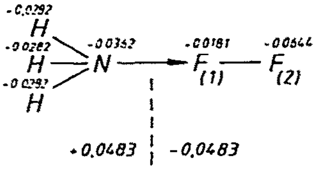
The quantum-chemical and the extended donor–acceptor approach have in common that they consider a molecular system as a whole [1]. Although the figures calculated by quantum-chemical methods depend on the assump-

TABLE 1

Calculated changes in atomic net charges and the amount of negative charge transferred from various donor molecules toward a chlorine molecule [15,16] using the Computer Program Gaussian 70 with an STO-3G basis set

Donor molecule	ΔH (kJ mol^{-1})	Pileup	Spillover	Transfer of charge
H_3N	4.30	−0.003	+0.030	0.008
Pyridine	3.45	−0.004	+0.026	0.005
HCN	1.95	−0.002	+0.018	0.001
H_2O	3.10	−0.366	+0.023	0.003

tions and on the approximations made, the results show the general trend of increased negative charge at the donor atom and of increased positive charge at the acceptor atom (Table 1). An example is provided of the work of Carreira and Person [14] on the interaction of an NH_3 molecule with a fluorine molecule



(v) Pileup and spillover effects in the light of the concept of electronegativity

In the preceding section the term "electronegativity" was used in the qualitative manner usually applied by chemists. In using this concept one should, however, always be aware of its conceptual and methodological limitations. Pauling defined electronegativity as the tendency of an "atom in a molecule" to attract electrons [17]. Although the properties of a given atom are known to be considerably altered by its molecular environment, this concept has been found most useful as a rule of thumb to describe bond properties and reactivities. In a diatomic molecule the atom which has a net negative charge is said to be more electronegative. On this qualitative basis, the specification of the electronegativity of an atom would amount to a specification of its position within a scale such that it would be negative in a diatomic molecule formed with any atomic species listed below it. Thus the criterion for setting up such a list of atomic species in the order of electronegativity would be the polarity and not the amount of the so-called "partial ionic bond character". As pointed out by Schwarzenbach [18] the polarity scale for the elements has been presented by Jakob Berzelius. His polarity scale is indeed essentially the same as Pauling's electronegativity scale.

For example, the formation of hydrogen fluoride from the atomic elements involves transfer of negative charge from the hydrogen atom toward the fluorine atom; the latter is therefore considered more electronegative. However, for its formation from hydrogen ions and fluoride ions charge transfer occurs in the opposite direction. Thus, the hydrogen ion acts as the species of greater electronegativity compared to that of the fluoride ion. Numerous suggestions have therefore been made in order to account for the dependence of electronegativity from its so-called state of "ionization" [19–32].

Mulliken [22] defined electronegativity as equal to the average of the ionization potential and the electron affinity. His values represent an average of a property over a range of ionization.

An attempt to approximate the energy E of an atom with N electrons present, $N = n - Z$, where Z is the atomic number and n the number of electrons around the nucleus at any particular state of "ionization", was made by Iczkowski and Margrave [32] by means of the expression

$$E(N) = aN + bN^2 + cN^3 + dN^4$$

For a given atom the E versus N plot (in which $N = 0$ corresponds to the neutral atom, $+1$ to an anion of negative unit charge and -1 to the cation of positive unit charge) has a given slope at the origin $(dE/dN)_{N=0}$. It will take electrons away from any atom which has a smaller slope, because in the process of doing so, the energy of the system as a whole will be lowered. Since this is the behaviour of the more electronegative atom toward a less electronegative atom, electronegativity is expressed by the slope $(dE/dN)_{N=0}$. The electronegativity of an ion would be given by the negative slope of the curve corresponding to the charge of that ion, for example $\chi_{Cl} = (-dE/dN)_{N=1}$.

For any states of atomic charges between $+1$ and -1 (except for zero), the slope of the curve is to represent the actual electronegativity (EN). Apart from the impossibility to define and to measure the actual net charge of an atom within its environment, it is a simplification to reduce the effects of the environment to a ficticious quantity. For various reasons it is impossible to define or to measure the actual net charge of an atom within its molecular environment.

However the following rules may be formulated: Increase in electronegativity is associated with increase in $\delta +$ or decrease in $\delta -$, respectively, whereas decrease in electronegativity is associated with decrease in $\delta +$ or increase in $\delta -$, respectively.

The term $\chi = -\partial E/\partial N$ may be considered as the net-charge regarding electronegativity. It is important to note that this term is equal to the respective chemical potential μ

$$-\partial E/\partial N = \chi = -\mu$$

From this follows also the electronegativity equalization mentioned above.

In order to account for the electronegativity changes in the course of an interaction, it would be important to know the actual net-charge of each of the atoms within the system. As these cannot be measured, a qualitative understanding of the changes involved may be desirable.

With regard to the changes involved in a donor–acceptor interaction, consider the system

$$H_3N + BF_3 \rightarrow H_3NBF_3$$

For transfer of negative charge from the donor toward the acceptor, the electronegativity of the acceptor should be greater than that of the donor. According to the rules given above, the loss of negative charge at the nitrogen atom would lead to an increase in *EN* at the N atom, and the gain in negative charge at the boron atom would decrease its electronegativity. As the electronegativity of N is increased, electronic charges are attracted from the H atoms, so that the *EN* of the N atom is decreased. The original decrease in *EN* at the B atom provides for charge transfer from the boron B to the fluorine atoms, so that the *EN* of the boron atom is again increased and that of the fluorine atoms decreased. Such changes will lead finally to electronegativity equalization, according to which the N atom would have been increased in electronegativity and the *EN* of the B atom decreased compared with the values in the isolated NH_3 or BF_3 molecules, respectively. According to this interpretation in the course of the interaction the net charge of the N atom as well as the positive net charge at the boron atom would have been decreased and neither a pileup nor a spillover effect would occur.

The alternative premise, namely that of greater *EN* of the nitrogen atom in NH_3 and of smaller *EN* of the boron atom of the acceptor component, seems to be in contrast to the actual transfer of negative charge from the donor to the acceptor component. On the other hand, chemists would prefer the idea of a greater *EN* of the N atom as compared to that of the B atom, even in the example under consideration. An interaction between nitrogen and boron atoms would then be expected to lead to a stable product by transfer of negative charge from the more electropositive boron atom toward the more electronegative nitrogen atom. In boron nitride the boron atoms are expected to carry (small) positive, and the nitrogen atoms negative, net charges [33].

A consideration of an appropriate Iczkowsky-plot illustrates that the interaction between NH_3 and BF_3 yields a stable product only if the electronegativity of the nitrogen atom is decreased and the electronegativity of the boron atom is increased.

As the net-charges of the nitrogen and boron atoms in the respective starting compounds are unknown, reasonable assumptions have been made in Fig. 1 as marked by N_1 and B_1. According to the greater electronegativity of the nitrogen atom in NH_3 compared with that of the boron atom in BF_3, the slope of the curve at N_1 is greater than that at B_1. In the course of the formation of a stable adduct, the electronegativity of the nitrogen atom must be decreased, i.e. it must acquire a point of its *EN*-curve with a smaller slope and the electronegativity of the boron atom must be increased, i.e. the point B_2 of the greater slope must be reached. In the stable adduct the said nuclei must reach such positions at their respective curves that their slopes have become equal. This requires the transfer of negative charge from the boron

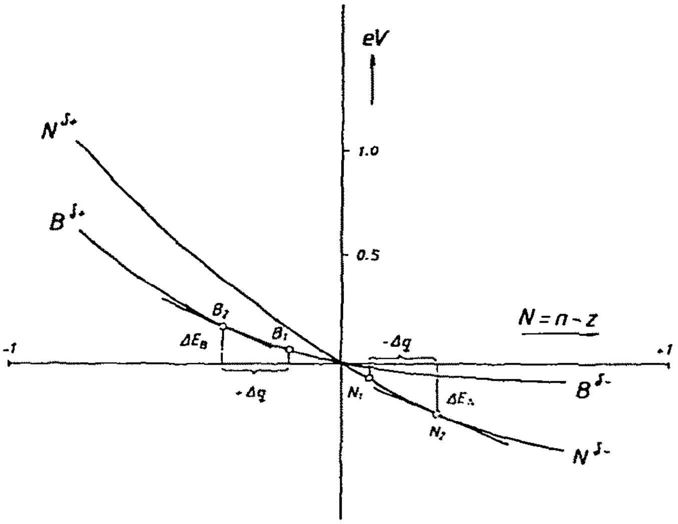


Fig. 1. Simplified illustration of the spillover and pileup effect by means of an E/N plot for the interaction between the boron atom of BF_3 and the nitrogen atom of NH_3.

atom toward the nitrogen atom. In this way the energy gained at the nitrogen atom ΔE_N is greater than the energy required at the boron atom ΔE_B.

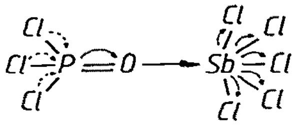
The charge transfer from the boron to the nitrogen atom leads to an increase of positive net-charge at the B atom and to an increase in negative net-charge at the N atom. These changes cannot be described by considering donor and acceptor atoms alone; they require the consideration of the charge-density rearrangements within the new molecular system under consideration, namely a pull of electrons toward the nitrogen atom (pileup) and a push of electrons from the boron atom (spillover).

It must be pointed out, however, that the reduction of the highly specific environmental effects to changes in hypothetical net-charges is bound to lead to nearly unsurpassable difficulties in other cases. For example, in the adduct $H_2O \cdot Cl_2$ the chlorine atoms will have different net-charges and yet their electronegativities should be the same (according to the requirement of electronegativity equalization). The authors hope to present a detailed account on such problems elsewhere.

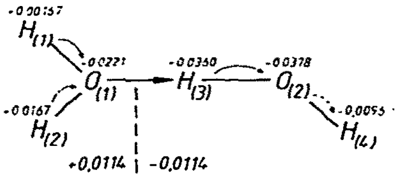
(vi) The second bond length variation rule

The changes in internuclear distances adjacent to the site of interaction induce subsequent changes in bond lengths throughout the system under consideration. Whereas a bond is lengthened when the electron shift occurs from the less electronegative toward the more electronegative atom, it is shortened when it occurs from the more electronegative to the less electronegative atom. In the latter case the bond polarity is decreased and the so-called covalent bond character increased.

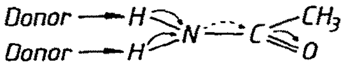
In the adduct $Cl_3PO \rightarrow SbCl_5$ the bonds adjacent to the donor–acceptor interaction are longer, but the Cl–P bonds shorter than in the free $POCl_3$-molecule [6].



Another interesting example is the charge density distribution in dimeric water compared to that in the free molecules. The results of an "ab initio SCF-calculation" [34] show the non-equivalence of three of the four hydrogen atoms in the dimeric unit. Whereas the $H_{(1)}$–$O_{(1)}$, the $H_{(2)}$–$O_{(1)}$, and the $H_{(3)}$–$O_{(2)}$ bonds are longer, the $O_{(2)}$–$H_{(4)}$ bond is shorter than in monomeric water (the electron shift occurred from the more electronegative toward the less electronegative atom [35]).



Interaction between a weak donor molecule and acetamide according to NMR evidence leads to a spillover effect at the hydrogen atoms of acetamide; the H–N bonds are lengthened and the N–C bond shortened. The interaction with a strong donor molecule, such as dimethylsulfoxide, leads to shortening of the N–C bond to such an extent that its rotability is lost, i.e. it attained double bond character, as evidenced from the non-equivalence of the two hydrogen atoms of the amino group [10].



(vii) Interactions involving chain molecules

In molecular systems, in which atoms of greater and smaller electronegativity are arranged in alternating succession, the structural variations caused by an intermolecular interaction are characterized by alternating bond lengthening and bond shortening. Acetamide has been mentioned as an example and the alternating changes in bond lengths in chloropropandiolcarbonate resulting from its interaction with $SbCl_5$ have been quoted several times [1–4]. It is also expected that in liquid water alternating bond lengthening and bond shortening will occur, resulting from dissolution of solutes [1,35,36].

The situation is, however, less obvious for systems containing arrays or clusters of atoms of the same kind. Seebach [37] has shown that in a chain of carbon atoms terminated by a C=O or a $C–NH_2$ group the donor properties are shown by the even-numbered carbon atoms and the acceptor properties by the uneven-numbered atoms. "Umpolung", i.e. exchange of the terminating donor group by an acceptor atom or group leads to exchange in properties between even-numbered and uneven-numbered carbon atoms.

Alternating properties of carbon atoms within aliphatic compounds have also been found to result from intermolecular interactions. Singh and Tedder [38] investigated the chlorination of alkylcarboxychlorides in the gas phase and in the presence of acceptor solvents. The interaction with the acceptor solvent with the COCl-group leads to alternating reactivities of the carbon atoms toward chlorination. The polarity of the C–H bonds is increased as the carbon atom has acquired a negative net-charge. This shows that the donor–acceptor interaction leads to alternating net-charges of the carbon atoms and hence to alternating lengthening and shortening of the C–C-bonds.

A further remarkable result is that the terminating C–H-groups have become most reactive, i.e. the hydrogen atoms have attained the greatest positive net charges of all hydrogen atoms attached to carbon atoms.

These findings are in accord with the expectations of the extended donor–acceptor approach according to which the greatest changes should occur not only at the donor and acceptor atoms themselves, but also at the atoms terminating the molecular system under consideration [1,2,4].

The interaction of ammonia with alkylboranes leads to increasing N–H, B–H, and B–C distances as well as to alternating shortening and lengthening of the subsequent C–C bonds as well as to shortening of the C–H bonds. The increase in negative net charge at the carbon atom of the terminating CH_3-group is greater in chains consisting of an uneven number of carbon atoms than in those of an even number. The spillover effect at the boron atom is greater the longer the aliphatic chain.

Likewise, the interaction of a BH_3-group with alkylamines leads to increasing B–H, N–H, and N–C distances, followed by alternating shortening and lengthening of the subsequent C–C distances; the C–H distances are slightly longer than in the alkylamines and the positive net charges greatest at the terminating CH_3-group.

Because a partial atomic charge can be neither defined nor measured, attempts have been made to circumvent this obstacle. For the above mentioned systems calculations have been made by means of the Sanderson method, the modified Sanderson method, the method of Jolly and Perry and by MO calculations of the SCF–CNDO type. The results may be summarized as shown in Fig. 2 [33].

Pileup and spillover effects were not found by semiempirical CNDO/2 and MNDO calculations. This is because the latter method does not consider the changes in internuclear distances involved, which appear intimately connected with the said effects. Unfortunately it has been impossible to carry out ab initio calculations for such big molecular systems. Calculations by the Jolly–Perry method and by the MO method confirmed the great influence of the changes at the donor and acceptor atoms on the calculated net charge of the C_1 atom; the latter is found in alkylboranes to become more negative by complexation and in alkylamines slightly more positive, in agreement with the increasing polarizations of the B–C and N–C bonds, respectively. The changes induced at the C_1 atom were found to depend on the chain length. The redistribution of charges extends throughout the molecular systems investigated (up to 10 carbon atoms); the greatest changes were found at the terminating C atoms which become more negative. As this effect is also strongly associated with a change in bond length, it is not found by the said MO calculations.

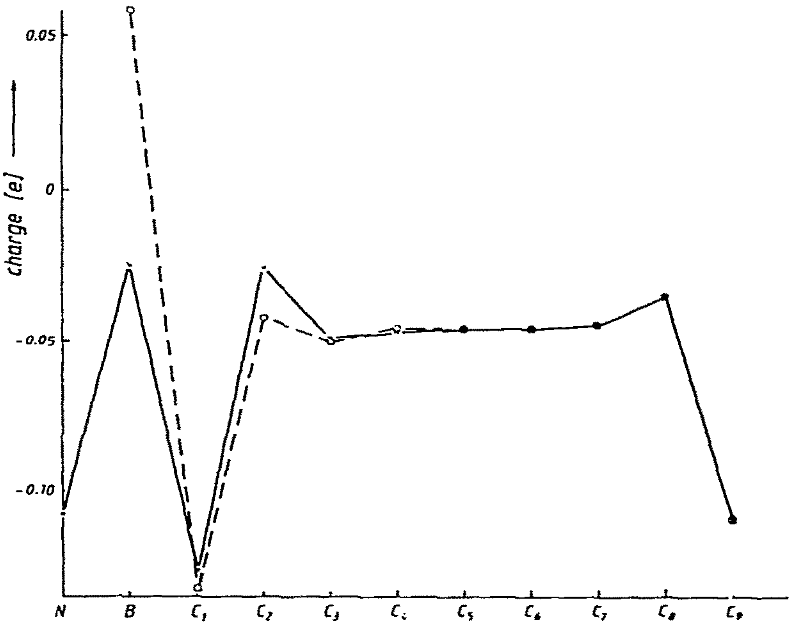


Fig. 2. Results of MO calculations by the SCF–CNDO-type according to the program kindly provided by Prof. P.G. Perkins [39], University of Glasgow. (------, charge distribution in nonylborane; ————, charge distribution in the ammonia adduct of the nonylborane.)

Another remarkable result is the alternating sequence of changes in net charges for the carbon atoms between C_1 and C_n.

C. STRUCTURAL VARIATIONS IN SOLUTION AS BASED ON STATISTICAL RESULTS

(i) Solvent effects

Solutes are known to be modified by interactions with the solvent. This means that the solvent is also modified by the presence of the solute. The solution represents a new molecular system, in which all of its constituent parts are interrelated and interdependent, and hence sharp border lines between solutes and solvent molecules cannot be drawn. Likewise, no border lines exist between "solvation shell" and "undisturbed" solvent molecules [1] which would be requested by the elementary electrostatic model, based on the idealization of the so-called "sphere in continuum"-model. Consequently, the parameters of the elementary electrostatic theory, namely the dipole moment or dielectric constant are of little value in order to account for the so-called "specific solvent effects".

The thermodynamic theory of solvation involves extrathermodynamic equations for the concentration dependence of thermodynamic functions, standard states of arbitrary nature, and additional complications encountered in passing from the study of solvation in solutions of non-electrolytes to solvation in ionic solutions because of the consequences of the interactions of the ions [40]. Models for the liquid state provided by statistical thermodynamics are based on massive approximations.

Despite the apparent wealth of experimental information, very few efforts have yet been made to characterize fully a number of aqueous systems and few of the experimental data originating from before 1955 can be utilized in basic studies of solution processes [41]. Much of the work was performed on fairly concentrated solutions and extrapolations to "infinite dilution" usually gave rise to incorrect values [42] and much of the work lacks experimental precision.

Various attempts have been made in order to characterize solvent effects by one empirical parameter, such as the Grunwald–Winstein Y-values [43], Kosower's Z-values [44], or Dimroth–Reichardt's E_T-values [45]. Each of them is able to account for relationship in a limited number of cases.

(ii) Donor number and acceptor number

The donor–acceptor approach requires the use of two empirical solvent parameters, namely one for the donor property and one for the acceptor

TABLE 2

Donor numbers (*DN*), acceptor numbers (*AN*) and dielectric constants (ϵ) for various solvents

Solvent	*DN*	*AN*	ϵ(*t*, °C)
Acetic acid	~10	52.9	6.2 (25°)
Acetic anhydride	10.5	–	22.1 (20°)
Acetone	17.0	12.5	20.7 (25°)
Acetonitrile (An)	14.1	18.9	38.0
Acetyl chloride	0.7	–	15.8 (22°)
Ammonia (liquid)	59	–	25 (−78°)
Benzene	~0	8.2	2.3 (25°)
Benzonitrile (BN)	11.9	15.5	25.2
Benzophenone	16	–	11.4 (50°)
Benzoyl chloride	2.3	–	23.0 (20°)
Benzoyl fluoride	2.0	–	22.7
Benzoyl cyanide	15.1	–	18.4 (20°)
Bromobenzene	<10	–	5.4 (25°)
Butanol	–	36.8	17.1 (25°)
t-Butanol	–	27.1	10.9 (30°)
t-Butylamine	57.5	–	–
n-Butyronitrile	16.6	–	20.3 (21°)
Carbon tetrachloride	0.0	8.6	2.2 (20°)
Chloroform	<10	23.1	4.8 (20°)
Chlorobenzene	<10	–	5.6 (25°)
1,2-Dichloroethane (DCE)	0.0	16.7	10.6 (20°)
Dichloroethylene carbonate	3.2	–	31.6
Dichloromethane	<10	20.4	9.1 (20°)
N,*N*-Diethylacetamide	32.2	–	–
Diethylamine	>50	9.4	3.6 (21°)
Diethyleneglycol dimethylether (diglyme)	24.0	10.2	–
Diethylether	19.2	3.9	4.3 (20°)
N,*N*-Diethylformamide	27	–	–
Dimethoxyethane	~20	–	–
N,*N*-Dimethylacetamide (DMA)	27.8	13.6	37.9 (25°)
Dimethylformamide (DMF)	26.6	16.0	36.7 (25°)
Dimethylsulfoxide (DMSO)	29.8	19.3	48.9 (20°)
N,*N*-Dimethylthioformamide (DMTF)	–	18.8	–
Dioxane	~19	10.8	2.2 (25°)
Diphenylphosphoric chloride	22.4	–	–
Ethanol	20	37.9	24.3 (25°)
Ethanolamine	>50	33.7	37.7
Ethylacetate	17.1	9.3	6.1 (20°)
Ethylamine	55.5	–	6.2 (25°)
Ethylene carbonate	16.4	–	89.1
Ethylenediamine	55.0	20.9	~14 (26°)
Ethylene glycol dimethylether (glyme)	~20	10.2	–
Ethylene sulphite (ES)	15.3	–	41.0

TABLE 2 (continued)

Solvent	*DN*	*AN*	$\epsilon(t, °C)$	
Formamide	24	39.8	109	(20°)
Formic acid	–	83.6	58.5	(16°)
Hexamethylphosphoric triamide (HMPA)	38.8	10.6	30.0	
Hexane	~0	~0	1.9	(20°)
Hydrazine	44.0	–	52.9	(20°)
Methanesulfonic acid	–	126.3	–	
Methanol	19.0	–	–	
Methyl acetate	16.5	10.7	6.7	(25°)
N-Methyl-ε-caprolactam (NMC)	27.1	–	–	
N-Methylformamide (NMF)	~27	32.1	182	(25°)
N-Methyl-2-pyrrolidone (NMP)	27.3	13.3	–	
N-Methyl-2-thiopyrrolidone	–	17.7	–	
Morpholine	–	17.5	7.3	(25°)
Nitrobenzene (NB)	4.4	14.8	34.8	(30°)
Nitromethane (NM)	2.7	20.5	35.9	(30°)
Piperidine	51	–	5.8	(22°)
Phenylacetonitrile	14	–	18.4	(20°)
Phenylphosphonic dichloride	18.5	–	26.0	
Phenylphosphonic difluoride	16.4	–	27.9	
Phosphorus oxychloride	11.7	–	14.0	
Propanediol-1,2-carbonate (PDC)	15.1	18.3	69.0	
Propanol	–	37.3	20.1	(25°)
iso-Propanol	–	33.8	18.3	(25°)
Propionitrile	16.1	–	27.7	(20°)
Pyridine (py)	33.1	14.2	12.3	(25°)
Selenium oxychloride	12.2	–	46.0	
Sulfolane (TMS)	14.8	19.2	42.0	(30°)
Sulphuryl chloride	0.1	–	10.0	(22°)
Tetrachloroethylene carbonate (TCEC)	0.8	–	9.2	
Tetrahydrofuran (THF)	20.0	8.0	7.6	(20°)
Tetramethylurea	31	–	–	
Thionyl chloride	0.4	–	9.3	(20°)
Toluene	~0	–	2.4	(25°)
Tributyl phosphate (TBP)	23.7	9.9	6.8	(20°)
Triethylamine	61.0	1.4	2.4	(20°)
Trifluoroacetic acid	–	105.3	8.4	(20°)
Trifluoroethanol	–	53.3	26.7	
Trifluoromethanesulfonic acid	–	129.1	–	
Trimethyl phosphate (TMP)	23.0	16.3	20.6	(20°)
Water	≥18.0	54.8	80.4	(25°)

property [1–4]. The parameters are known as the donor number DN [1,46] and the acceptor number AN [2,47], respectively (Table 2). Numerous quantitative relationships have been found between these solvent parameters on the one side and thermodynamic, kinetic, and structural parameters on the other side [4,48].

LFER have been established for example between the donor number and the free enthalpies of transfer for cations [2], the chemical NMR-shifts of cations [2], the basicity parameters B based on the frequency shift of the O–D vibrations in monomeric $CH_3O{-}D$ [49], the ionization constants of trimethyltin iodide and other halides [50], the rate coefficients of various organic reactions, such as the interaction of benzylbromide and pyridine [49]. Relationships have also been found between the acceptor number and the free enthalpies of transfer for anions, the Y-values, the Z-values, the E_T-values [2], the polarographic half wave potentials of anions, and the rates of S_{N^1} and solvolysis reactions [4,51]. It may be added, that the rates of S_{N^2} reactions are decreased as the acceptor number of the solvent is increased [51,52].

The following rules have been given with regard to choosing the appropriate solvent for a particular interaction [2]:

(1) For the production of reactive anions, such as carbanions, a solvent of high donor number and of low acceptor number is advised.

(2) For the production of reactive cations, such as carbonium ions, a solvent of high acceptor number and of low donor number is suggested.

(3) In order to achieve the formation of stable ions and to carry out ionic interactions, the solvent should have both a high donor number and a high acceptor number.

(iii) Quantum chemical support for donor and acceptor numbers

Fair linear relationships have been found between the donor number and the energy of the highest occupied molecular orbital (HOMO) as well as between the acceptor number and the energy of the lowest unoccupied molecular orbital (LUMO) [53].

Calculations have been carried out by the SCF ab initio approximation, using the STO–3G minimal basis set, on the available geometries of a number of solvent molecules.

Free enthalpies of transfer for the potassium ion show about the same relationship with either HOMO energies or the DN (Fig. 3). Likewise, the free enthalpies of transfer for a given anion, as related to the AN [2] show an analogous correlation to the LUMO energies (Fig. 4) [53].

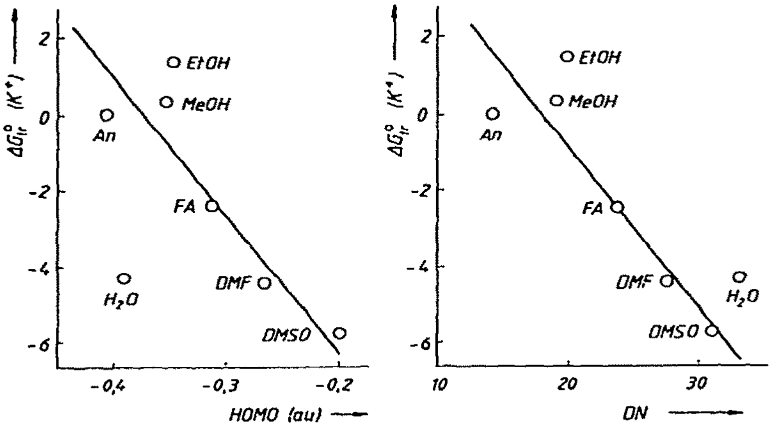


Fig. 3. Free enthalpies of transfer (acetonitrile as reference solvent) for K^+ versus the solvent HOMO eigenvalues and versus solvent donor number, respectively, in different solvents [53].

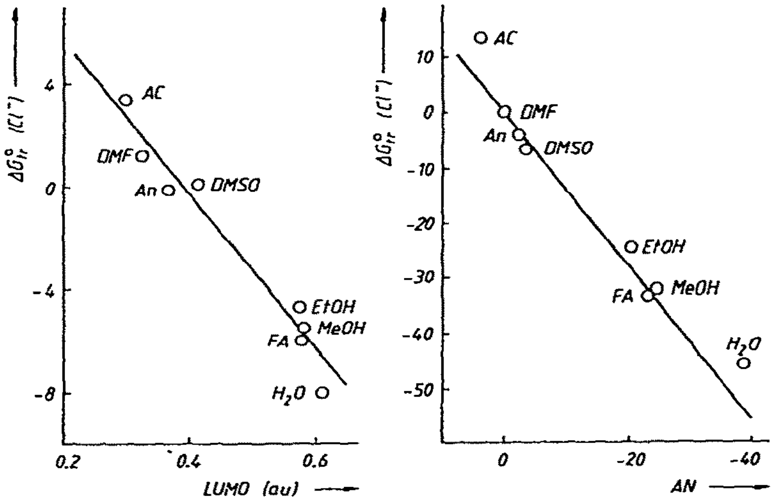


Fig. 4. Free enthalpies of transfer (acetonitrile as reference solvent) for the chloride ion versus the solvent LUMO eigenvalues and versus the solvent acceptor number, respectively, in different solvents [53].

(iv) Semiempirical models

A two-parameter approach involving DN and E_T-values has been suggested by Krygowski and Fawcett [54]. An attempt to provide a more rigorous basis of solvent effects on chemical reactions has been undertaken by Mayer [55,56]. His approach involves three parameters, namely the donor number, the acceptor number, and the free energy of evaporation of the solvent.

$$\Delta G^0 = a\,\Delta \mathrm{DN} + b\,\Delta \mathrm{AN} + c\,\Delta G^0_{\mathrm{vp}}$$

The last term is related to the free energy required to create holes in the solvent and hence to overcome the solvent–solvent interactions. These become more important in highly structured solvents, i.e. in solvents of highly developed amphoteric properties.

Applications have been shown of solubilities of alkali metal salts, complex equilibria, ion association equilibria and of kinetic phenomena in various non-aqueous solutions.

(v) A relationship between empirical solvent parameters and the dielectric constant

In order to account quantitatively for the equilibrium constants of ionization phenomena in solution, the role of the dielectric constant cannot be overlooked [50]. It has been suggested that the ionization of a covalent substrate by a solvent occurring according to the two subsequent steps should be considered:

(1) Heterolysis by coordinating solute–solvent interactions with formation of ion-associates.

(2) Electrolytic dissociation of the ion-associates [50].

The first step is related to the solvent donor number and to the solvent acceptor number, whereas the second step is related to the dielectric constant of the medium.

An interesting approach has been put forward by Schmid [57] in relating the dielectric constant ϵ to the amphoteric properties of the solvent. For aprotic solvents he obtained a relationship between $\log \epsilon$ and a linear combination of the donor number and the acceptor number by means of a least square multiple regression analysis. In this way the following equation was found:

$$\log \epsilon = 0.0771(\mathrm{AN}) + 0.0054(\mathrm{DN}) + 0.2581$$

This relationship is shown for 29 solvents in Fig. 5. Thus, the dielectric constant is more strongly influenced by the acceptor property than by the donor property of the solvent. For example, triethylamine has a very high DN, but a very low AN; its dielectric constant is also low. Otherwise, anhydrous hydrogen cyanide has a high dielectric constant but low donor properties; however, its acceptor properties seem fairly well developed.

It is remarkable that, at least for aprotic solvents, the dielectric approach and the empirical solvent parameters according to the donor–acceptor approach has been, roughly, brought under one umbrella.

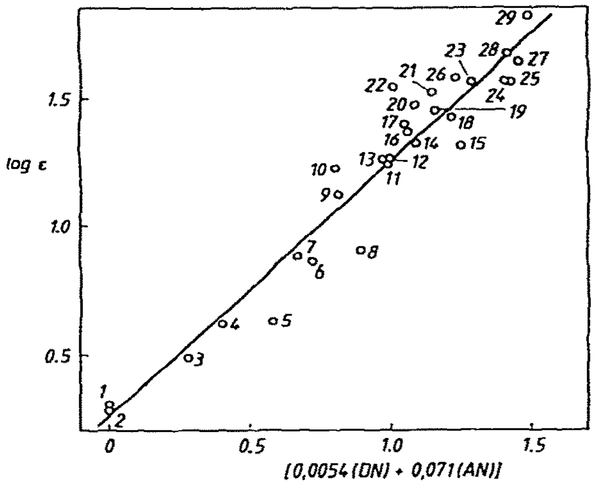


Fig. 5. Plot of log ε versus $0.0054(DN)+0.071(AN)$ for the following solvents: 1, hexane; 2, cyclohexane; 3, dibutylether; 4, diethylether; 5, anisole; 6, glyme; 7, tetrahydrofuran; 8, tributylphosphate; 9, 3,3-dimethylbutanone; 10, 3-pentanone; 11, acetophenone; 12, butanone; 13, cyclohexanone; 14, acetone; 15, trimethylphosphate; 16, tetramethylurea; 17, benzonitrile; 18, propionitrile; 19, nitroethane; 20, hexamethylphosphoric triamide; 21, N-methylpyrollidinone; 22, nitrobenzene; 23, dimethylformamide; 24, nitromethane; 25, acetonitrile; 26, dimethylacetamide; 27, sulpholane; 28, dimethylsulfoxide; 29, propanediol-1,2-carbonate [57].

Of course, all of the correlations involving empirical solvent parameters may be used only as rules of thumb. In this way they are very useful, but they do not serve the purpose of providing a deeper understanding of each individual solution system (see section D).

(vi) Structural variations of solutes

The bond length variation rules of the extended donor–acceptor approach are very useful in accounting for the structural changes of solutes in a given solvent. The solute particles are modified by the properties of the solution. Hence the structural changes depend not only on the pure solvent but rather on the solution properties, which are modified by the solutes present. This means solute concentration and presence of other solutes are important in accounting for the changes of a solute structure due to its environment. In dilute solutions the liquid environment is usually approximated by that of a "pure" solvent. For example, the ^{23}Na NMR chemical shift of sodium perchlorate is linearly related to the solvent donor number, whereas no such relationship is found for sodium halides because of the structural influences of the halide ions on the cation properties [58,59]. The increase in electron density at an atomic cation, caused by the donor actions of the solution, is also found at the coordination centre of a robust complex cationic species. For example, in trisethylenediaminecobalt(III)-perchlorate solution the donor solvent interacts with the hydrogen atoms of the NH_2-groups. This leads to lengthening of the N–H bonds (first bond length variation rule) and to shortening of the N–Co bonds (second bond length variation rule), which means decreasing positive net charge at the cobalt coordination centre [60]. This is seen from the ^{59}Co NMR chemical shift, which is related to the solvent donor number. An analogous relationship is also found when the solvent donor number is plotted versus the polarographic half wave potential which is related to the standard redox potential [60,61]. This means that the redox potential is related to the structural changes at the redox-active centre as expressed by the changes in the ^{59}Co NMR chemical shift (Fig. 6). The standard redox potential is a measure for the activity of the redox-active species. Differences in activities in different solvents are therefore related to differences in electron densities at the redox-active centre as expressed by the differences in NMR chemical shift [61].

This structural explanation for the thermodynamic activities in solution may also hold for the interpretation of the observed differences in activities for a given solute in a given solvent at different concentrations. The charge densities at the redox-active centre are changed as the solute–solvent and solute–solute interactions mediated through solvent molecules are varied. It may be emphasized that the structural changes due to changes in either solvent or solute concentration are not expressed in the familiar representation of a chemical reaction [61].

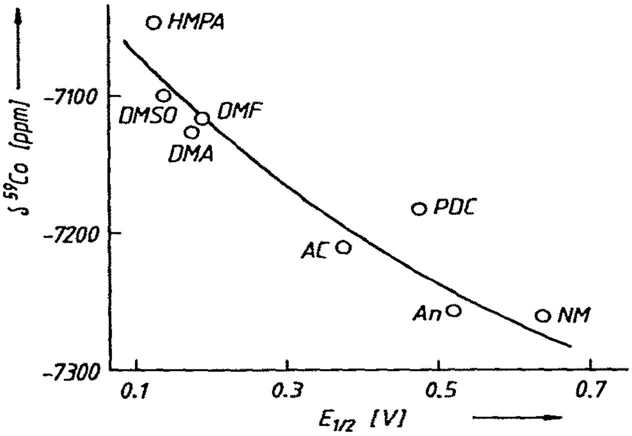
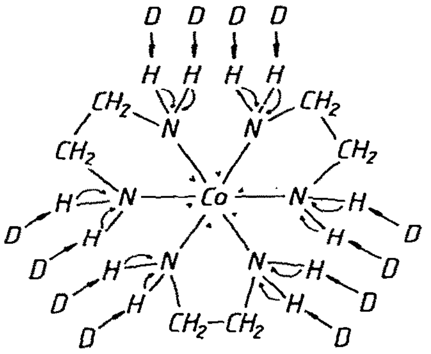


Fig. 6. Relationship between halfwave potentials versus bisbiphenylchromium(I/O) and the ^{59}Co n.m.r. chemical shifts of trisethylenediaminecobalt(III)-perchlorate referred to a 0.4 M aqueous $K_3Co(CN)_6$ solution as external reference in the aprotic solvents.



Whereas redox potentials of Fe(tmphen)$_3$(II/III) (tmphen = [3,4,7,8]tetramethyl-1,10-phenanthroline) in various aprotic solvents are hardly influenced by the coordinating properties of the solvents [62], the redox potentials of Fe(niphen)$_3$(II/III) (niphen = 5-nitro-1,10-phenanthroline) show a significant decrease with increasing donor number of the solvent. This has been explained by nucleophilic attack of solvent molecules at the coordination centre. This explanation is consistent with the known solvent and salt effects on the dissociation rates of ferroin and ferriin in aqueous solution [62]: strong nucleophiles such as hydroxide ions, cyanide ions, or azide ions may directly interact with the coordination centre, thereby weakening the Fe–N bonds resulting in an increase in the rate of dissociation; weak nucleophiles do not attack at the coordination centre.

(vii) Structural variations of the whole solution

The modification of solutes by the solvent molecules implies that the solvent is also modified by the solutes. Such modifications are usually considered for the solvent molecules near the solute particles, i.e. for the so-called solvation spheres. Because a border line between solvation sphere and less affected solvent molecules cannot be drawn, information on solvation is frequently obtained by indirect methods, such as from crystalline hydrates. In solution, the interactions between solute and solvent molecules are mediated through the solvent spheres and the structural changes have a collective character, i.e. they are connected with the correlated behaviour of solutes and solvents [61,63]. However, statistical information available for properties of the whole solution cannot lead to distinctions between different solvent molecules. All statistical data, for example the intensities or frequencies in vibrational spectra, the broadening of the bond widths at one half maximum adsorbance, X-ray data, or NMR results yield time and space averages over all solvent molecules of the solution. Proton NMR studies cannot distinguish between hydrogen atoms of water, the dissolved acid, and those of hydrogen ions and hydroxide ions.

The question is, therefore, in what ways may the enormous amount of information be disclosed that is disguised in the accessible data. This is a fundamental problem which must be solved in order to obtain an understanding of the highly differentiated and concerted actions which are continuously taking place within the liquid system.

D. WHAT STATISTICS DO NOT DISCLOSE—THE STRUCTURAL VARIABILITY IN MICROSCOPIC REGIONS AND THE HIERARCHIC ORDER

(i) Philosophical background

As atoms and molecules have no definable border lines (in agreement with quantum-mechanical conclusions), they are subject to characteristic mutual "penetrations" and hence they are differentiated. It is extremely unlikely to find ions or molecules within a molecular system in precisely the same energy states at any given time [1]. According to statistical procedures the differences in properties are reduced to mean quantities and these are attributed equally to the different parts. The existence and the reactions of a real system require, however, non-statistical behaviour in microscopic areas.

In attempting to take an alternative point of departure the authors no longer start from hypothetical models on solvent structures or from ideally pure solvents (which do not exist) but rather from a given real solution. They propose to consider the differences of the constituent parts carefully and to attempt to learn about their interrelationships and their significance within the real system under consideration.

Such an approach must integrate all available information from any reliable source and must be comprehensive in every respect. Because it would be impossible to gain knowledge on several aspects of the real system at any given time, the system cannot be understood from its multiplicity. We therefore try to learn to understand the system in its multiplicity in that each of the aspects is considered in its complex relationships within the undivided and non-idealized whole object [13,61,64–69].

In order to recognize the differences of the parts within the real system, the authors:

(1) Consider each phenomenon in its static and dynamic aspects from various points of view.

(2) Take into consideration all environmental effects accessible.

(3) Order all pieces of evidence with regard to the whole system under consideration.

(ii) Structural aspects due to hydration in water

The rules of the extended donor–acceptor approach are based on statistical information and they have been applied in a statistical sense so far. In order to illustrate the structural changes in a solution due to the addition of solute particles these rules are applied to regions in molecular dimensions.

Local structural changes in water may be described as due to the introduction of a solute particle. Around an atomic cation the water molecules are coordinated by means of their oxygen atoms, which function as electron donors toward the cation. This leads to a decrease in positive net charge Δq_M^+ for the cation. According to the bond length variation rules, the negative net-charge of the oxygen atoms of the coordinated water molecules is increased (pileup). Both the loss in positive net charge at the metal ion Δq_M^+ and the gain in negative net-charge of the oxygen atoms Δq_O^- is counterbalanced by appropriate losses in positive net-charges of the hydrogen atoms [61]

$$\Delta q_M^+ + \sum \Delta q_O^- = \sum \Delta q_H^+$$

This means that the O–H bonds have been increased in polarities and lengthened. Formation of the second hydration sphere leads to further charge redistributions: the said O–H bonds are further lengthened, the $M \leftarrow O$ bonds shortened with further decrease in positive net-charge at the coordination centre. The O–H bonds in the second hydration sphere have become longer, but still shorter than those in the first hydration sphere. As further hydration layers are established, a charge density pattern with the following structural features is produced.

With decreasing distance from M^+ the intermolecular $O\cdots O$ distances are shortened, whereas the intramolecular O–H bonds are lengthened. This means the hydrogen bonds approach linearity and symmetry as they come close to the coordination centre. In fact, local density gradients appear to exist, as has been pointed out by Lengyel [70]. The static aspects of this pattern may be compared to that produced by waves on a water surface originating from the point where a stone has been thrown in.

At any time a characteristic pattern of inhomogeneities is established throughout the liquid system. In a solvent mixture there are even inhomogeneities in analytical composition. For example, in a water–alcohol mixture, containing a nickel salt, water molecules are found enriched near the metal ion [71], whereas alcohol molecules are enriched in the regions remote from the ions. A quantum-chemical study has shown that the modifying effect on the solvent structure appears to extend up to 150 water molecules [72]. An experimental indication for effects reacting up to 2 μm is the solubility of quartz in capillaries of extremely small cross-section [73]. Resolution of data into solvation and excess properties reveals that the latter do not vanish at $c \approx 10^{-6}$, which means a sphere of influence of each ion of about 100 nm, corresponding to about 400 water layers [74].

A consideration of the linear relationships between activation energy and entropy of activation (the so-called compensation effect) leads Likhtenstein [75] to the conclusion that the solvent transmits the change in the state of its molecules caused by the cooperative interactions of solute and solvent molecules to adjacent solvent molecules, so that even weak interactions extend over large ensembles and make contributions to the energy and entropy terms.

In this way even surface molecules must be affected and hence the solution may be considered as one giant molecular system. The local contraction around solute particles should also cause contractions within the liquid surface. This may be the reason why a vapour pressure of a solution is lower than that of a pure solvent.

The macroscopic properties of a solution may be changed even by small changes of the environment (pressure, temperature) or composition of the solution. Small changes in the latter may cause measurable changes in bulk properties, such as vapour pressure, surface tension, viscosity, density, or conductivity.

Solute particles appear, therefore, to exert a decisive influence on the solution structure. They are modified by the solvent and they modify the solvent structure in characteristic ways. They may therefore be considered as "structure modified and modifying" centres, or abbreviated "SMM-centres" [1]. They are known to migrate within the solution according to the gradients in chemical potentials, which never vanish. Under equilibrium conditions the migrations must be dynamically ordered, as the properties of the system are maintained by them.

(iii) Structural aspects due to the presence of holes

Liquid water is known to contain a considerable amount of "empty" space, usually referred to as "voids" or "holes". The existence of mobile holes [76] requires the presence of "inner surface" areas. A surface is known to be under strain and the mean intermolecular distances shorter than within bulk areas [77]. The static aspects of the arrangement of water molecules surrounding a hole of a dimension as is known to exist in certain clathrate compounds has been illustrated in an idealized two-dimensional way [78] in Fig. 7.

Like a vacancy in a solid material [64–67], a void in a liquid is a SMM-centre. The various SMM-centres within a given liquid, i.e. solutes and holes, are not independent from each other but rather interrelated even when

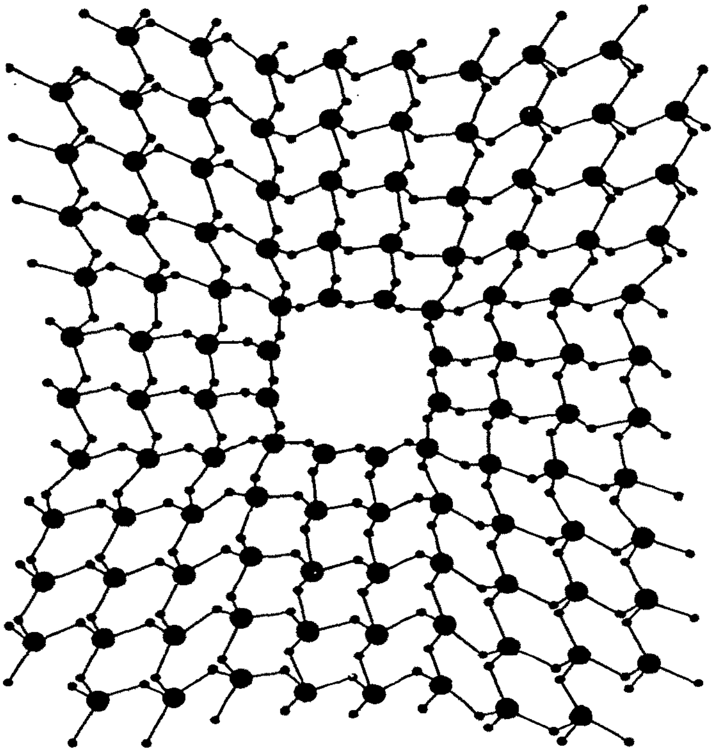


Fig. 7. Illustration of the static aspects of order of water molecules surrounding an idealized hole of a dimension as found in certain clathrate compounds [78].

separated by many layers of solvent molecules.

It is well known that dissolved particles of a given molecular species are differentiated within a given system. Whereas thermodynamic parameters represent mean values for all particles under consideration, the activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ refer only to those particles of the reacting species which are in preferred states for the interaction. Such parameters are particularly sensitive to changes in environment.

(iv) Structural aspects of phase boundaries

Molecules at the phase boundaries are under an enormous strain and in states of relatively high energies (surface tension). The number of SMM-centres is known to be greater within the boundary areas the greater the local surface curvature [79]. Although the liquid surface appears macroscopically smooth it is microscopically highly differentiated.

It has been shown that donor–acceptor interactions between molecules lead to great effects at the peripheries of the interacting molecules. Likewise, the presence of solutes or other SMM-centres has far-reaching effects, which are well-pronounced at the phase boundaries. A phase boundary cannot be considered only as part of the phase under consideration, as it is continuously and specifically interacting with the contacting phase. The phase boundary has a two-fold function, namely to separate different phases and to connect them at the same time.

Interactions between different phases at phase boundaries may be described by the donor–acceptor approach. Part of the charges of solute particles are distributed over the surface molecules. Donor–acceptor interactions between the phases lead both to pileup and spillover effects at the respective phase boundaries and hence to the development of an electric double layer, even in the absence of ionic species. This means that an interface is bound to be in a more or less pronounced state of tension, and this is a requirement for the co-existence of the contacting phases [13]. The state of tension is maintained dynamically, but the individual processes cannot be measured or predicted. The motions appear chaotic, although the maintenance of an equilibrium state requires ordered relationships as established by local gradients in chemical potential.

(v) The concept of hierarchic order

In order to understand the continuous motions by which the system maintains its configuration and integral operation in an essentially constant environment in favour of optimal preservation of its integrity, the ordered relationships between the parts within the system have to be investigated.

According to the local and temporal significance of the parts within the system, the points made in the preceding sections may be summarized as follows.

Distinctions may be made between "normal" solvent molecules, SMM-centres (solute ions, solute molecules, voids), and molecules or ions at surfaces [61]. In each of these groups the parts serve the whole solution in different ways.

The mean relaxation times, the mean energies per part, the strain to which the molecules are subjected decrease in the order boundaries > SMM-centres > "normal" solvent molecules. The constituent parts influence each other in different intensities, due to their mutual penetrations, in such ways that the differences in domination become apparent, which allows recognition of successively graded levels, as they are characteristic for a so-called hierarchic order recently proposed for the solid state [65–67]. A level is hierarchically higher the greater its significance for the whole system. Forces operative at a higher level control and regulate more strongly the properties of the parts which serve on one of the lower levels than vice versa. All of the motions within the system appear to be consequence and illustration of the concerted actions of dynamic forces, which , like a field, are not directly observable.

In establishing a hierarchy of significance among the constituent parts of the real solution under consideration, the surface molecules must certainly be appropriated a prime position. They provide the first line of defence, they show greatest adaptabilities towards changes, they are under greatest strain, and in states of highest energy. The surface regulates the exchange of matter, energy, and information for the whole system. Its dynamic interactions both with the bulk phase and with its environment require that each point of the surface contains information of the static and dynamic aspects of the system as "seen" from the point under consideration.

Redistribution of energy, matter, and information is controlled and regulated by the forces acting on the system. Interactions between surface and other parts of the system are taking place continuously according to ordered relationships. New holes may be produced and existing holes may be annihilated by the surface areas. The holes are under the decisive influence of the forces acting at the surface; surface particles are distributed in the liquid as influenced by the forces acting at the surface.

Thus, SMM-centres are serving the system on a level inferior to that of the surface. The migrations of SMM-centres follow gradients in chemical potentials with simultaneous formation of new such gradients in other areas. Neither the local analytical composition nor the positions of solute particles and holes remain constant, but rather the regularities of their ordered relationships.

The decisive influences of solutes and of voids on a great number of solvent molecules cannot be questioned. Both the static and the dynamic aspects in the so-called solvation spheres are under the decisive influence of the SMM-centres. The far-reaching effects are usually neglected, although their existence cannot be denied. Solvent molecules are therefore more or less influenced by the forces which operate on higher levels; this means that solvent molecules serve the lowest level within the hierarchic order of the system under consideration.

In each of the said hierarchic levels, namely (i) boundaries, (ii) SMM-centres, and (iii) "normal" solvent molecules, the parts serve the system in an optimal way: the parts in the lower levels have more "freedom", but their influence on the system properties is small.

Even within each level the parts may differ from each other in their significance for the whole system. In the surface level areas of high local curvature and those connected to inner surface areas appear to be hierarchically superior to the flat microregions.

Likewise, solute particles, even those of the same kind, differ from each other according to their differences in local environment. Holes may differ in shape and properties and in particular those connected with the surface appear hierarchically higher than smaller and more isolated holes. Their properties are also influenced by nature and number of the solute particles. By diluting a solution, the number of solute particles is diminished, whereas the number of holes is hardly affected. The holes are therefore fulfilling dynamically preserving functions and hence they are hierarchically higher than the solute particles.

The differentiation of "normal" solvent molecules is also obvious. Solvent molecules in the so-called "solvation spheres" are hierarchically superior to those in the less differentiated areas, which are found more remote from other SMM-centres.

The various regions are never separated from each other, but rather in co-existence by dynamic interrelationships. A characteristic motion pattern is maintained, which is independent from the actual positions of the particles. As such regularities are established, we may speak of a "dynamic order", which cannot be directly observed. We may describe, however, in what ways the dynamic order makes use of the various parts within the complex relationships of the system.

It is the dynamic order which determines the properties of the parts. Knowledge of the parts is insufficient in order to account for the dynamic order. It is therefore not possible to learn by purely analytical methods about the ordered relationships, because these are lost by the physical or mental dismemberment of the complex system [80].

The dynamic order provides the framework for the highly differentiated vibration pattern; the shorter an internuclear distance, the greater is the frequency and the smaller the amplitude. The vibrations of the various parts are determined by all energetic influences. What is termed "thermal vibrations" is actually a complicated dynamic pattern with a character all of its own that reflects all energetic influences, including that of "temperature".

The only access to the dynamic order is the systematic study of macroscopic properties and their changes due to changes in environment. For a given system relationships appear to exist between changes in properties, such as vapour pressure, surface tension, viscosity, density, reaction rates, conductivity, mechanical properties, etc. and applied changes in environmental conditions, such as temperature, pressure, irradiation, molecular environment, action of fields, or mechanical forces. Only a few of such relationships appear to be well-established and most of them have been hardly investigated so far. It should be corroborated, in what ways the changes in macroscopic properties are related to microevents and to changes in microregions. We may have to learn to understand in what ways the parts in the various levels contribute to a given macroscopic property, in what ways changes in energy are distributed over the various hierarchic levels, and in what ways the energies per part and the numbers of parts per level, i.e. the thermodynamic and activation properties, are varied as the environment is changed. This should lead to a deeper understanding of the dynamic interactions which are taking place continuously within the complex system of the given solution.

E. CONCLUSIONS

The extended donor–acceptor approach has been shown to provide a universal framework for nearly all kinds of molecular interactions. The structural changes due to changes in environment have been expressed by the so-called bond length variation rules. These have been shown to be well supported by the results of quantum-chemical calculations and to be in agreement with the refined concept of electronegativity.

With regard to solution chemistry the empirical solvent parameters, i.e. donor and acceptor number, proved very useful, and they were recently shown to be related to the HOMO and LUMO energies, respectively. A further relationship has been found between them and the dielectric constant. Whereas the properties of the dissolved species may be neatly characterized by the experimentally accessible mean values, fundamental difficulties are encountered in the attempts to attack the problem of solution structures in this way.

The authors have therefore undertaken the unfamiliar and difficult task of attempting to interpret data disguised by statistical results. In choosing the real solution as the point of departure, we were led to the concept of the hierarchic order of matter, as proposed recently for the solid state.

The concept of hierarchic order is not in competition with existing views, nor is it antithetical to them. The apparent differences result from the different starting points, which are bound to lead to different questions and to different answers. The new approach is therefore bound to disappoint all those who are looking for quick answers to the problems at hand.

Molecular science was developed enormously by the rigorous and exclusive application of the particle model of matter. Although quantum mechanics implies the continuum aspects of matter, further development was characterized by its concentrating on quantitative, and hence on the discontinuum (particle), aspects.

The dynamically ordered relationships as expressed by the concept of the hierarchic order, require the recognition of the continuum aspects of matter. In this way it is hoped to provide a qualitative understanding of reality in its multiplicity and hence to open a new access to molecular science. Questions may be raised which would not have been expected from our present views.

The basic problem of the inherent interrelationships and interdependencies of discontinuum aspects of matter shall be considered in a forthcoming paper.

ACKNOWLEDGEMENTS

Thanks are due to the Fonds zur Förderung der wissenschaftlichen Forschung in Österreich for the support of the investigations.

REFERENCES

1 V. Gutmann and G. Resch, Z. Chem., 19 (1979) 406.
2 V. Gutmann, The Donor–Acceptor Approach to Molecular Interactions, Plenum, New York, 1978.
3 W.B. Jensen, The Lewis Acid Base Concept–an Overview, Wiley, New York, 1980.
4 V. Gutmann, Electrochim. Acta, 21 (1978) 661.
5 J. Gažo, I.B. Bersuker, J. Garaj, M. Kabešová, F. Kohout, H. Langfelderova, M. Melnik, M. Serator and H. Valach, Coord. Chem. Rev., 19 (1976) 253.
6 I. Lindqvist, Inorganic Adduct Molecules of Oxo-Compounds, Springer-Verlag, Berlin, 1963.
7 V. Gutmann, Rev. Roumaine Chim., 22 (1977) 619.
8 G.A. Bowmaker and S. Hacobian, J. Aust. Chem., 21 (1968) 551.
9 S. Ichiba, H. Sakai and H. Negita, J. Chem. Phys., 54 (1971) 1627.
10 G. Gonzalez-Moraga, private communication, 1980.
11 K. Burger and E. Fluck, Inorg. Nucl. Chem. Lett., 10 (1974) 171.
12 W. Horill and H. Noller, Z. Phys. Chem. (Frankfurt am Main), 100 (1976) 155.
13 G. Resch and V. Gutmann, Z. Phys. Chem. (Frankfurt am Main), 126 (1981) 223.
14 L.A. Carreira and W.B. Person, J. Am. Chem. Soc., 94 (1972) 1485.
15 J. La Grange, L. Leroy and G. Louterman-Leloup (1977) (reference in ref. 1).
16 L. Leroy and G. Louterman-Leloup, J. Mol. Struct., 28 (1975) 33.
17 L. Pauling, The Nature of the Chemical Bond, Cornell University Press, New York, 1960.
18 G. Schwarzenbach, Chimia, 28 (1974) 101.
19 W. Gordy, Phys. Rev., 69 (1946) 604.
20 H.O. Pritchard and H.A. Skinner, Chem. Rev., 65 (1955) 745.
21 A.L. Allred and E.G. Rochow, J. Inorg. Nucl. Chem., 5 (1958) 264.
22 R.S. Mulliken, J. Chem. Phys., 2 (1934) 782.
23 A.D. Walsh, Proc. R. Soc. London, Ser. A, 207 (1951) 13.
24 W.J. Gordy, J. Chem. Phys., 19 (1951) 792.
25 R.T. Sanderson, J. Chem. Phys., 23 (1955) 2467.
26 R.T. Sanderson, Chemical Periodicity, Reinhold, New York, 1960.
27 J.C. Craver, R.C. Gray and D.M. Hercules, J. Am. Chem. Soc., 96 (1974) 6851.
28 W.E. Swartz, R.C. Gray, J.C. Craver, R.C. Taylor and D.M. Hercules, Spectrochim. Acta, Part A, 30 (1974) 1561.
29 W.L. Jolly and W.B. Perry, J. Am. Chem. Soc., 95 (1973) 5442.
30 W.L. Jolly and W.B. Perry, Inorg. Chem., 13 (1974) 2686.

31 W.L. Jolly and W.B. Perry, Discuss. Faraday Soc., 54 (1972) 13.
32 R.P. Iczkowski and J.L. Margrave, J. Am. Chem. Soc., 83 (1961) 3547.
33 W. Linert, Dissertation, Technical University of Vienna, 1981.
34 D. Hankins, J.W. Moskowitz and F.E. Stillinger, J. Chem. Phys., 53 (1970) 4544.
35 V. Gutmann, E. Plattner and G. Resch, Chimia, 31 (1977) 431.
36 G. Resch and V. Gutmann, in T. Bertini et al. (Eds.), Advances in Solution Chemistry. Plenum, New York, 1981.
37 D. Seebach, Angew. Chem., 91 (1979) 259.
38 H. Singh and J.M. Tedder, J. Chem. Soc. B, (1966) 605.
39 P.G. Perkins, private communication, 1979.
40 H.L. Friedman and C.V. Krishnan, in F. Franks (Ed.), Water—A Comprehensive Treatise, Vol. 3. Plenum Press, New York, 1963.
41 J.S. Rowlinson, in F. Franks (Ed.), Water—A Comprehensive Treatise, Vol. 2. Plenum Press, New York, 1963, p. 1959.
42 J. Barthels, private communication, 1980.
43 E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70 (1948) 846.
44 E.M. Kosower, J. Am. Chem. Soc., 78 (1956) 5700; 80 (1958) 3253, 3261, 3267.
45 K. Dimroth, C. Reichhardt, T. Siepmann and F. Bohlmann, Liebigs Ann. Chem., 661 (1963) 1.
46 V. Gutmann and E. Wychera, Inorg. Nucl. Chem. Lett., 2 (1966) 257.
47 U. Mayer, V. Gutmann and W. Gerger, Monatsh. Chem., 106 (1975) 1235.
48 U. Mayer, Monatsh. Chem., 108 (1977) 1479.
49 A.G. Burden, G. Collier and J. Shorter, J. Chem. Soc., Perkin Trans. 2, (1976) 1627.
50 V. Gutmann and U. Mayer, Monatsh. Chem., 100 (1969) 1048.
51 A.J. Parker, U. Mayer, R. Schmid and V. Gutmann, Org. Chem., 73 (1978) 1843.
52 U. Mayer, Monatsh. Chem., 109 (1978) 775.
53 A. Sabatino, G. La Manna and L. Paoloni, J. Phys. Chem., 84 (1980) 2641.
54 T.M. Krygowski and F.R. Fawcett, J. Am. Chem. Soc., 97 (1975) 2143.
55 U. Mayer, Pure Appl. Chem., 51 (1979) 1697.
56 U. Mayer, Monatsh. Chem., 109 (1978) 421.
57 R. Schmid, private communication, 1981.
58 R.H. Erlich and A.I. Popov, J. Am. Chem. Soc., 93 (1971) 5620.
59 M. Herlem and A.I. Popov, J. Am. Chem. Soc., 94 (1972) 1431.
60 G. Gonzalez-Moraga, U. Mayer and V. Gutmann, Inorg. Nucl. Chem. Lett. 15 (1979) 155.
61 V. Gutmann and G. Resch, Pure Appl. Chem., 53 (1981) 1447.
62 U. Mayer, A. Kotocova and V. Gutmann, J. Electroanal. Chem., 103 (1979) 409.
63 G. Maisano, P. Migliardo and F. Wanderlingh, J. Chem. Phys., 69 (1978) 676.
64 V. Gutmann and G. Resch, Acta Chim. Hung., 106 (1981) 115.
65 V. Gutmann and G. Resch, Rev. Inorg. Chem., 2 (1980) 93.
66 G. Resch and V. Gutmann, Z. Phys. Chem. (Frankfurt am Main), 121 (1980) 211.
67 G. Resch and V. Gutmann, Abh. Braunschweig. Wiss. Ges., 30 (1980) 38.
68 V. Gutmann and G. Resch, Abh. Friedrich Schiller-Universität, Jena, 1981, p. 100.
69 V. Gutmann and G. Resch, 31st Meet. Int. Soc. Electrochem. Venice, 1980, Extended Abstracts, Vol. 1, 359.
70 S. Lengyel, Acta Chim. Hung., 37 (1963) 87.
71 W.J. MacKeller and D.B. Rorabacher, J. Am. Chem. Soc., 85 (1971) 3903.
72 B.M. Rode, S. Fujiwara and R. Fukikura, private communication, 1980.
73 D. Schuller, Naturwissenschaften, 60 (1973) 145.
74 J. Barthel, private communication, 1981.

75 G.I. Likhtenstein, Russ. J. Phys. Chem., 44 (1970) 1079 (Engl. transl.).
76 Z.G. Szabó, Acta Chim. Hung., 40 (1964) 275.
77 V. Gutmann and H. Mayer. Rev. Inorg. Chem., 1 (1979) 51.
78 G. Resch and V. Gutmann, in I. Bertini, L. Lunazzi and A. Dei (Eds.), Advances in Solution Chemistry, Plenum Press, New York, 1981.
79 R. Defay, I. Prigogine, O. Bellmans and D.M. Everett, Surface Tensions and Adsorption. Wiley, New York, 1966.
80 P.A. Weiss, The Science of Life. Futura, New York, 1973.