Forschung, Wissenschaft

Ion Pairing and Outer Sphere Effect *

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Summary

Ion-ion and ion-solvent interactions are presented from the point of view of the donor-acceptor concept. The solvent donor properties are characterised by the donor number and the solvent acceptor properties by the acceptor number. Formation of ions is considered as a substitution reaction. It is suggested to apply the terms "ion-pair» and "ion-association" only as long as the ions retain essentially their structural identies. Various processes hitherto referred to ion pairing or ion association are re-interpreted in terms of "outer-sphere"-complexation. The outer-sphere effects are formulated for the changes in inner-sphere bond distances. They are applied to various ion-ion interactions, such as $[Fe(CN)_6]^{3-}$. $[Bu_4N]^+$. The inconsistencies of the "contact ion pair"-concept are demonstrated including its application to phenomena involving hydrogen bonding. A simplified reaction scheme based on the donor-acceptor concept is presented for ion-ion as well as for ion-solvent interactions.

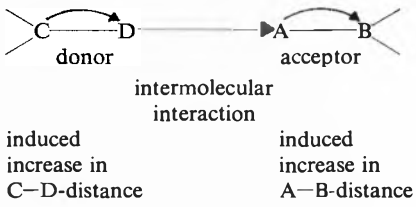
List of abbreviations and symbols

AC	Acetone	Et	Ethyl
Acc	Acceptor	Fl	9-Fluorene
AN	Acceptor Number	HMPA	Hexamethylphosphoric triamide
An	Acetonitrile		
B	Base	μ	Dipol Moment
Bu	Butyl	Me	Methyl
D	Donor	NB	Nitrobenzene
DMA	Dimethylacetamide	PDC	Propanediol-1,2-carbonate
DME	Dimethoxyethane		
DMF	Dimethylformamide	py	Pyridine
		Pr	Propyl
DMSO	Dimethylsulfoxide	S	Solvent
DN	Donor Number	sv	solvated
$E_{1/2}$	Polarographic Half wave potential	TBAP	Tetrabutylammonium perchlorate
ε	Dielectric Constant	TEAP	Tetraethylammonium perchlorate
en	Ethylene diamine	THF	Tetrahydrofuran
EPA	Electron pair acceptor	TMS	Tetramethylene sulfone
EPD	Electron pair donor		
ES	Ethylene sulfite		

1. Ionization, Free Ions and Ion Pairs

The concept of ion pairs has been introduced 50 years ago by Bjerrum [1] in order to account for conductivities of eletrolyte solutions lower than expected from the electrostatic theory. The ionic species are surrounded by tight solvation shells, which are hardly affected by the formation of the ion pairs, as these are weakly connected and can be separated by increasing the dielectric constant of the medium. The associated species are also termed "solvent-separated ion pairs [2] in order to distinguish from "contact ion pairs", which do not meet the phenomenological criteria mentioned above, as considerable changes in the charge density distributions are taking place in the course of their formation. An ion may be defined as an atom or a molecule which carries either positive or negative charges. The term ion will be applied to any such species as long as interionic interactions do not alter the structure significantly; e.g. the charged entity can be considered as retaining its identity in "ion-association".

According to the extended donor-acceptor concept an intermolecular interaction is expected to lead to an increase in bond length of the bonds adjacent to the area of intermolecular attack [3]. Within a given system the induced increase in intramolecular bond length is a function of the intermolecular distance established:



The extent of the intermolecular interaction may be characterised by the ΔG-value for the interaction. The increase in bond distances is also reflected in characteristic changes in spectroscopic properties, as well as in chemical behaviour, such as redox or kinetic properties. The intermolecular interaction depends both on the nucleophilic and the electrophilic properties of the reactants, which may be characterized by the donor number [4] (or donicity) and the acceptor number [5] respectively. The donor number DN is defined as the negative ΔH-value for the 1 : 1 interaction of the electron pair donor EPD towards $SbCl_5$ in dilute solution of 1,2-dichloroethane [4]:

$$DN \equiv -\Delta H_{EPD.SbCl_5}$$

The acceptor number has been deduced from the ^{31}P

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n.m.r. chemical shift of triethylphosphinoxide in the presence of the electron pair acceptor [5] (EPA):

$Et_3\overset{\curvearrowright}{P}=O \rightarrow EPA$

The δ-values have been referred to hexane, corrected for the difference in volume susceptibilities and extrapolated to infinite dilution. The chemical shift of the compound $Et_3P = O - SbCl_5$ dissolved in 1,2-dichloroethane was taken as 100 and all other δ-values converted accordingly.

Table 1: Donicity and Acceptor Number for Selected Solvents

Solvent	*DN*	*AN*
Acetic Acid	–	52.9
Acetone (AC)	17.0	12.5
Acetonitrile (An)	14.1	19.3
Acetylchloride	0.7	–
Benzene	–	8.2
Benzonitrile (BN)	11.9	15.5
Benzoylchloride	2.3	–
Carbontetrachloride	–	8.6
Chloroform	–	23.1
Diethylether	19.2	3.9
Dichloroethylenecarbonate	3.2	16.7
Diglyme	≈ 24.0	10.2
Dimethylacetamide (DMA)	27.3	13.6
Dimethylformamide (DMF)	24.0	16.0
Dimethylsulfoxide (DMSO)	29.8	19.3
Dioxane	14.8	10.8
Ethanol	19.0	37.1
Ethylene Sulfite (ES)	15.3	–
Hexamethylphosphoric triamide (HMPA)	38.8	10.6
Methanol	20.0	41.3
Nitrobenzene	4.4	14.8
Nitromethane	2.7	20.5
Propanol	18.0	33.5
Propylencarbonat (PDC)	15.1	18.3
Pyridin (py)	33.1	14.2
Tetrahydrofuran	20.0	8.0
Tributylphosphate	23.7	–
Water	18	54.8

Unfortunately no values have been made accessible for ionic species, and their coordinating properties may vary considerably in different solvents.

A strong intermolecular interaction may lead to heterolysis of one of the bonds with formation of (solvated) ions [6]:

$D + A - B + Acc \rightleftarrows D \rightarrow A \cdots B \rightarrow Acc \rightleftarrows DA^+ \cdot B^- \cdot Acc$

The formation of solvated ions from a covalent substrate may be represented in a simplified way as follows [6, 7]:

(1) $A - B + Solvent \rightleftarrows A^+_{sv} \cdot B^-_{sv}$; K_{form}

The higher the dielectric constant of the medium, the greater is the chance for separation of the solvated ions: [6, 7]

(2) $A^+_{sv}B^-_{sv} \rightleftarrows A^+_{sv} + B^-_{sv}$; K_{sep}

(1) represents the formation of ion pairs (K_{form}) primarily dependent on the coordinating interactions between solute and solvent and (2) their dielectric separation into free ions (K_{sep}), which is mainly a function of the dielectric constant of the medium.

The dissociation constant K_{diss} for the overall process formulated as

$A - B + solvent \rightleftarrows A^+_{sv} + B^+_{sv}$; K_{ion}

is equal to the product of the equilibrium constants of the constituent equilibria [5]:

$K_{diss} = K_{form} \cdot K_{sep}$

In a medium of high dielectric constant, such as water, the concentration of associated ions is neglegibly small; K_{form} and K_{sep} cannot be measured separately. On the other hand, in solvents of low dielectric constant there will be practically no dissociation and the ionized substrate will be present nearly exclusively as associated ions, such as solvent-separated ion pairs. In solvents of medium dielectric constant, K_{form} and K_{sep} may be determined separately by combination of appropriate experimental techniques [6, 7]. For example, spectrophotometry may be applied in order to obtain the total concentration c_I of ionized substrate

$c_I = c_{A^+_{sv}} \cdot c_{B^-_{sv}} + c_{A^+_{sv}}$

whereas the concentration of free ions $c_{A^+_{sv}}$ may be determined conductometrically. With c_o denoting the analytical concentration of the solute one obtains [7]:

$c_o = c_{AB} + c_{A^+_{sv}} \cdot c_{B^-_{sv}} + c_{A^+_{sv}} = c_{AB} + c_I$

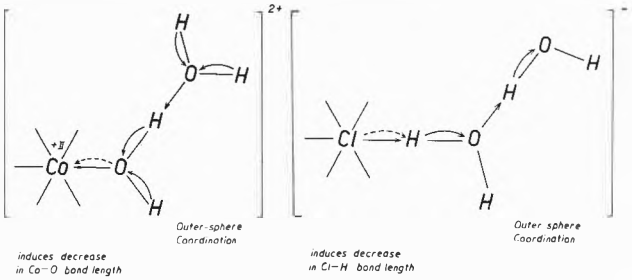
$$K_{form} = \frac{c_I - c_{A^+_{sv}}}{c_I - c_I}; \qquad K_{sep} = \frac{c^2_{A^+_{sv}}}{c_I - c_{A^+_{sv}}}$$

The situation may be illustrated by comparing the electrolytic dissociation behaviour of lithium halides and tetrabutylammonium halides in PDC (DN = 15, ε = 65) and HMPA (DN = 38,8, ε = 30) [8]. The lithium halides are associated in HMPA, although the comparison of the dielectric constants would suggest opposite behaviour. HMPA is strongly coordinated to the Li^+-ion and hence lithium halides are completely ionized with formation of tightly solvated cations, while in PDC (lower donor properties) lithium halides are incompletely ionized and partly present as unionized species [8] (to which more recently the term "contact-ion pair" is applied). These are in equilibrium with free ions, since due to the high solvent dielectric constant all associated ions are dissociated. Unlike lithium halides, tetrabutylammonium halides are fully dissociated in PDC, while they are associated in HMPA and this is in agreement with simple electrostatic considerations [8].

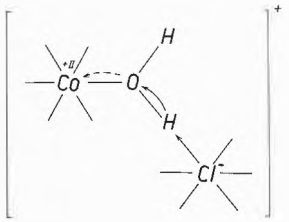
2. Outer-sphere Complexes

Werner [9] has introduced the concept of outer-sphere complex formation for the interactions of coordinatively saturated complex ions with further ligands [10]. The donor-acceptor approach describes the formation of outer-sphere solvation in the following way [3, 11]:

Coordination of water molecules in the inner-sphere of a cation leads to an increase in O–H-bond length and hence to an increase in acidity of the hydrogen atoms. "Free" water molecules interact preferentially with the latter providing electrons from the oxygen atoms. In this way an additional transfer of negative charge towards the coordination center is effectuated by which the inner-sphere coordinate bond length is decreased: *Outer-sphere coordination leads to decreasing inner-sphere bond lengths.* Anions are hydrated by means of inner-sphere hydrogen bonds. The charge transfer from the anion to the oxygen atom of the coordinated water molecule leads to an increase in basisity, which favours outer-sphere coordination. In this way additional charge is removed from the anionic coordination center [12] with decrease in inner-sphere anion—hydrogen bond length [11].



By increasing the solute concentration the hydration layers are partly removed *and* the hydration layers may be penetrated by ions of opposite charges, for example



This reaction may be considered as displacement of solvent molecules by partly desolvated ions in the outer-sphere solvation layers.

This type of species is frequently considered a solvent separated ion pair [13, 14], although it differs remarkably in properties from those of the former species. Differences are found in spectroscopic, in redox and kinetic properties as well as in dissociation behaviour. While the former are separated by increasing the dielectric constant of the medium, the latter remain combined under these conditions. As the ions have lost their identity by this process, it appears advisible to avoid the term "ion pair" or "ion association" and to denote this species as an outer-sphere complex involving ions of opposite charges.

The reaction

$$[Co(OH_2)_pCl(HOH)_q)]^+ + (n+m)H_2O \rightleftarrows \rightleftarrows [Co(OH_2)_{n+p}]^{2+}[Cl(HOH)_{m+q}]^-$$

is formally analogous to the ionization of any other covalent substrate.

Thus, the association constants of $[Co(en)_2Cl_2]^+Cl^-$ in different solvents [15] represent the formation constants of the outer-sphere complexes, rather than those of ion pairs as there are no relations between "association constant" and solvent dielectric constants or the dipole moments. Instead they depend both on the donor and the acceptor properties of the solvent. In the process

$$[Co(en)_2Cl_2]^+_{sv} + [Cl]^-_{sv} \rightleftarrows [Co(en)_2Cl_2]Cl$$

solvent molecules coordinated in the outer-sphere of the complex ion are to be replaced by a chloride ion. The smaller the solvent donicity, the greater is the ease of its replacement. In order to compete successfully with the donor solvent molecules, the donor properties of the solvated chloride ions should be stronger. As they are decreased by increasing solvation, this replacement is supported by decreasing solvent acceptor number [16]. Hence the formation constant of $[Co(en)_2Cl_2]Cl$ is greater the smaller both the donicity and the acceptor number of the solvent:

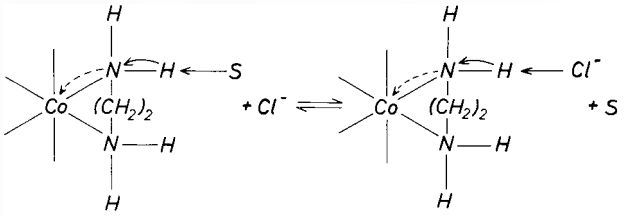
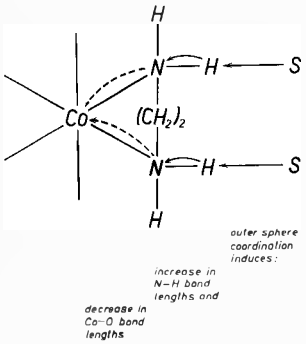


Table 2: Formation constants for the one-to-one outer-sphere complex between $[Co(en)_2Cl_2]^+$ and Cl^- [15]

Solvent	K_{form} [$mol^{-1} \cdot l^1$]	*DN*	*AN*	ε	μ [Debye]
Methanol	150	19,0	41,3	32,6	1,71
DMSO	400	29,8	19,3	46,68	3,90
DMF	8000	26,6	16,0	36,71	3,86
DMA	20000	27,8	13,6	37,78	3,81
TMS	42000	14,8	19,0	43,3	4,81

The increase of the association constants (table 2) in the order methanol, DMSO, DMF and DMA primarily reflects the decreasing electrophilic solvent properties. If MeOH had a higher *DN*, K_{form} would be even smaller. The high value of the association constant in TMS is mainly due to its low donicity which facilitates substitution outer-sphere coordinated solvent molecules by the strongly coordinating chloride ion.

The outher-sphere effect to cations has been convincingly demonstrated by the results of polarographic measurements on $[Co(en)_3]^{3+}$ in solvents of different donicity [17]: increasing donicity was found to shift the half-wave potential to more negative values (table 3): Increasing stability of the outer-sphere complex is due to the electron donation from the outer-sphere solvent molecules to the redoxactive coordination center:

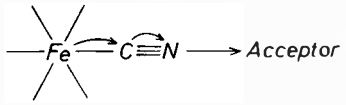


In this way the oxidizing properties of the Co(III)-species are lowered to a greater extent than the reducing properties are increased in the Co-(II)-species.

Table 3: Polarographic half wave potentials of $[Co(en)_3][ClO_4]_3$ in different solvents

Solvent	$E_{1/2}$ [V]	*DN*	ε
NM	+ 0.61	2.7	35.9
BN	+ 0.44	11.9	25.2
AN	+ 0.46	14.1	38.0
Acetone	+ 0.23	17.0	20.7
DMF	+ 0.18	26.6	36.1
DMSO	+ 0.12	29.8	45.0

The existence of outer-sphere complexation to anions has been clearly demonstrated by recent polarographic measurements: The half wave potentials for the reduction of hexacyanoferrate(III) to hexacyanoferrate(II) in aprotic solvents are shifted to more positive values the greater the acceptor number of the solvent [18].



Since in the reduced state the nitrogen atoms of the coordinated ligands are more basic than in the oxidized state, the former are more strongly stabilized by outer-sphere interaction with a given acceptor and this results in a shift to more positive potential values [18]. It is even more remarkable that in a given solvent the half wave potential is highly influenced by the nature of the cation of the supporting electrolyte. The potential values are significantly different for the tetraethylammonium and for the tetrabutylammonium [19]. This behaviour cannot be explained by electrostatic ion-ion interactions. Instead the tetraalkylammonium ions are considered to compete for coordination at the N-atoms with solvent molecules. The differences in redox potential express the differences in electron transfer from the redox-active center. Since the potentials are found at more positive values for the Et_4N^+, this acts clearly as a stronger acceptor than the Bu_4N^+ ion. This statement is in accordance with the differences in half wave potentials for these two ions in different solvents: In a weak acceptor solvent, such as DMF the differences are greater than in a strong acceptor solvent such as methanol [19], as replacement of solvent molecules is favoured by increasing acceptor properties of the cation as well as by decrease in acceptor properties of the solvent molecules.

Table 4: Half wave potentials for the reduction $[Fe(CN)_6]^{3-} - [Fe(CN)_6]^{4-}$ in 0.1 M solutions of tetrabutylammoniumperchlorate (TBAP) and tetraethylammonium perchlorate (TEAP) respectively in different solvents at 25 °C

Solvent	$E_{1/2}$ [V] TEAP	TBAP	$\Delta E_{1/2}$ [V]	*AN*	ε
DMF	− 0.31	− 0.61	0,30	16	36,7
AN	− 0.28	− 0.42	0,14	18,9	36,0
DMSO	− 0.27	− 0.39	0,12	19,3	46,7
PDC	− 0.17	− 0.20	0,03	18,3	65,0
NM	− 0.07	− 0.14	0,07	20,5	36,7
EtOH	+ 0.30	+ 0.24	0,06	37,1	24,3
MeOH	+ 0.47	+ 0.38	0,09	41,3	32,6

In this respect it is of interest to note that n.m.r. measurements on solutions of tetramethylammonium salts of $[Fe(CN_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ in water showed contrary to electrostatic expectations, that ion pair formation with the latter was very modest as compared with the former [20]. According to the donor-acceptor concept this is due to the competition of the weakly acidic Me_4N^+-ions with the more strongly acidic water molecules. Since the reduced species binds stronger than the oxidized species, coordination of water molecules in the reduced form prevents coordination of the cations more effectively than in the oxidized form, where the ≡N–HOH bonds are appreciably weaker.

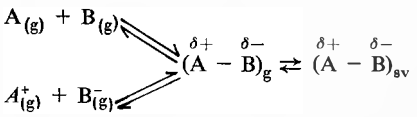
3. The Concept of Contact Ion Pairs

It has been unfortunate, that the application of the Debye-Hückel theory to aqueous solutions has tempted organic chemists to think along similar lines: This aim appears to have been supported by the failure to characterise ionization phenomena in organic solvents by a single parameter, such as Kosower's *Z*-values [21] Winstein's *Y*-values [22] or Dimroth and Reichardts E_T-values [23]. The recently presented "Two Parameter Approach" [24] has revealed that these values are fair measures of the electrophilic solvent properties rather than the "solvent polarity" or the "ionizing properties".

Winstein suggested the concept of "contact ion pairs" or "intimate ion pairs" in order to explain the stereochemical course of solvolysis and of electrophilic substitution reactions [25]. Since then the existence of both types of ion pairs has been widely accepted and supported by various experimental results [2, 26–29].

It is evident that the properties of a bond between two atoms do not depend on its mode of formation. For example the properties of the H–F-molecule will not allow a decision whether it has been formed from the

atoms or from hydrogen ion and fluoride ion. Hence solvation in a particular solvent is also independent from its history and it will always lead to an increase in bond distance compared to that in the gaseous state [3]. In such cases it is impossible to distinguish by experiment a solvated contact ion pair from the unionized solvated species [30].



Justice [30a] has pointed out that it is impossible for a contact-ion pair to be stable in a continuum where ions are approximated as unpolarizable hard spheres. There are only a few borderline cases to which this approximation is justified and for these the term "contact-ion pair" may be retained, e.g. where the "sphere in continuum model" can be applied, and where the unsolvated ions do not lose their identities in forming non-conducting entities. Examples are $[Bu_4]^+[BPh_4]^-$ in water or KF in benzene in the presence of a crown-ether.

In all other cases a contact ion pair is indistinguable from the unionized species and the formation of solvated ions is not a function of the dielectric constant, but rather of the coordinating solvent properties [24], which may be characterized by empirical parameters, namely the *DN* for the nucleophilic and the *AN* for the electrophilic properties [5, 24].

In alkali metal-fluorenyl compounds the extent of ionization depends on the acidic properties of the alkali metal ion and the solvent donicity rather than on the solvent dielectric constant [2] (table 5).

Table 5: Amount of solvent-separated ion pairs (+ free ions) of alkali metal salts of 9-fluorene (Fl) in various EPD-solvents at 25°

Solvent	% Solvent-separated ion pairs (+ free ions)				
	DN	ε	Li^+Fl^-	Na^+Fl^-	Cs^+Fl^-
dioxane	15	2.2	0	0	–
toluene	0.1	2.4	0	–	–
2-Me THF	20	6.3	25	0	–
THF	20.0	7.6	75	5	0
DME	20	7.2	100	95	0
DMSO	29.8	45.0	100	100	–
pyridine	33.1	12.3	100	100	–

The lithium compounds are more readily ionized than the other alkali metal compounds, the ionization being enhanced by increase in solvent donicity (table 5).

Structural evidence reveals that in the solid lithium fluorenyl THF-adduct the carbanionic electron pair is bonded to the lithium despite the delocalization of the aromatic system [31]. The ionization of naphthalene sodium is drastically decreased by changing from DME ($DN \approx 24$) to THF ($DN \approx 15$) [32–34].

The variations in IR-bond frequency on changing the anion, as observed in THF [35, 36] and acetone [37] cannot be ascribed to the rather low dielectric constants of these solvents, but they are due do their moderate solvating powers. In a strong donor solvent such as DMSO [38, 39] or pyridine [40] the frequencies are nearly independent from the anion. Nearly constant frequencies independent from the anion are found for Li-salts in mixtures of benzene and dimethylsulfoxide, ranging in dielectric constant from 7 to 46, as lithium ions are preferentially coordinated by DMSO-molecules [39, 41] irrespective the dielectric constant of the medium.

Likewise in a solution of lithium fluorenyl in mixtures of acetone and nitromethane [37] the lithium ion is preferentially solvated by acetone. Raman and NMR results, which were interpreted by means of the concept of contact ion pairs at low acetone content are consistent with the presence of the unionized lithium compound.

A very remarkable relationship exists between solvent donicity and chemical shift of the ^{23}Na nucleus in solutions of sodium perchlorate in various donor solvents [42, 43]. The influence of the concentration of iodide ions—interpreted as contact ion pairs—is due to outer-sphere coordination of Na^+_{sv} by iodide ions.

It has been mentioned that the limiting case of the existence of "contact ion pairs" may be found in salts of hardly solvated ions in media of medium or low dielectric constant. Table 6 shows that this concept cannot be applied to tetraalkylammonium halides in solvents of well-developed acceptor properties [16].

Table 6: Ion-pair association constants of tetraalkylammonium halides

Solvent	MeOH [44]	EtOH [45]	Prop. [45]	CH_3CN [46–48]	DMF [49]	NB [50, 51]
ε	32,62	24,33	20,45	36,02	36,71	34,69
μ [Debye]	1,70	1,70	1,66	3,96	3,86	4,03
Me_4NCl	7	122	456	56		
Me_4NBr	14	146	638	46	37	
Me_4NI	18			19	14	
Et_4NCl						80
Et_4NBr	10	99	373		16	62
Et_4NI		133	466	8	12	29
Pr_4NCl						
Pr_4NBr	6	78	270	4	12	
Pr_4NI	17	120	391	5	8	
Bu_4NCl		39	149			
Bu_4NBr	3	75	266	2		56
Bu_4NI	16	123	415	3	8	27

For these compounds specific solute-solvent interactions are restricted to those between anion and solvent. The association constants of the halides in the alcohols decrease in the order $I^- > Br^- > Cl^-$ contrary to expectations from the electrostatic theory. (The Born solvation energies cannot be made responsible

for this trend, as the reverse trend is found in solvents of higher dielectric constant, namely in CH_3CN, NB and DMF). The behaviour in the alcohols is readily explained by increasing solvation by H-bonding in the order $I^- < Br^- < Cl^-$. In aprotic solvents the gas phase stability order is retained at least for salts with small tetraalkylammonium ions [16].

4. Interactions Involving Hydrogen Bonding

The elementary electrostatic description of hydrogen bonding is rather unsatisfactory [52]. Relevant structural questions such as that of the energetically most favourable arrangement of molecules in aggregates or that of the stereochemistry of hydrogen bridges have been shown to be answered successfully in a semi-quantitative way by the LCAO-MO methods [52]. The comparison of the results of ab initio and of semi-empirical LCAO-MO-calculations suggests that the CNDO/2 procedure can provide a qualitatively correct presentation of hydrogen bonding, which is in accordance with the donor-acceptor concept.
For example in nitrobenzene tetrabutylammonium picrate is present as unassociated ions [53], while for the tributylammonium salt in the same solvent the association constant is 526. This is due to the presence of a hydrogen atom in the latter salt hence capable to hydrogen bonding to the anion. Likewise the formation of carbanions by deprotonation of an acid can be considered as due to stabilization of the hydrogen ion by coordination of the base [26]:

$$B + H - CR_3 \rightleftarrows B \rightarrow H \cdots CR_3 \rightleftarrows BH^+ + CR_3^-$$

Recent evidence on the substitution equilibria of quinuclidine hydrochloride and n-butylamine hydrochloride rejects the concept of contact ion pairing [54]. In these cations the hydrogen atom bonded to the nitrogen is sufficiently acidic to undergo hydrogen bonding not only with the chloride ion, but also with solvent molecules. The replacement reaction

$$R_3NH^+ \leftarrow Cl^- + n\,S \rightleftarrows [R_3NH \leftarrow S]^+ + [Cl(S)_{n-1}]^-$$

"contact ion pair"

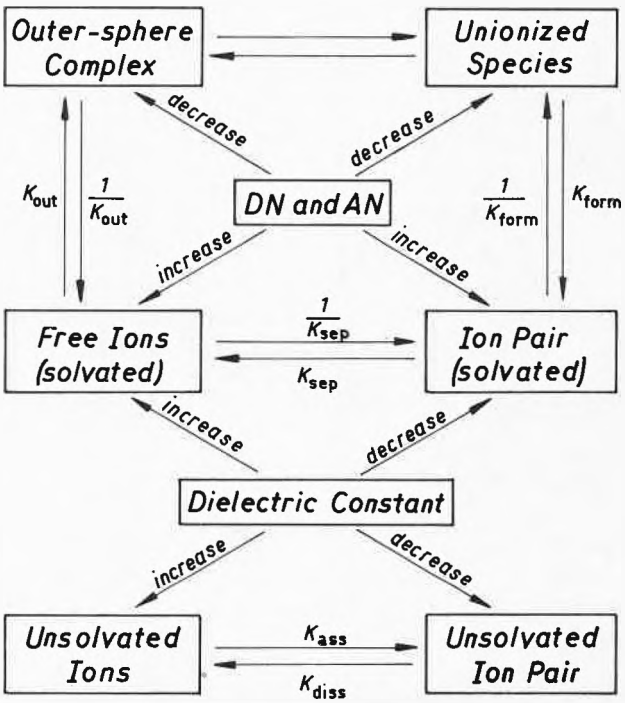
involves the destruction of the "contact ion pair" with formation of a hydrogen bond with a neutral solvent molecule [54]. The extent of this replacement reaction is not a function of the dielectric constant or of the dipole moment of the medium, but it is dependent on both the donor- and acceptor properties of the solvent molecules: The greater the solvent donicity, the more readily is the chloride ion replaced by the solvent molecules; the greater the acceptor number, the greater is the stability of the solvated chloride ion and the smaller its ability to form the ionionized species (the "contact ion pair") (table 7).
Likewise the dissociation constant of triethylammonium picrate is 40 times greater in acetonitrile ($DN = 14.1$) than in nitrobenzene ($DN = 4.4$) [55].

Table 7: Ionization Constants K_{Ion} of quinuclidinium chloride (QHCl) and of n-butylammonium chloride (Bu_4NH_3Cl) in different solvents

Solvent	K_{Ion} QHCl	$BuNH_3Cl$	*DN*	*AN*	ε (25 °C)	μ [D]
DMSO	$1{,}2 \cdot 10^{-2}$	$1{,}2 \cdot 10^{-2}$	29.8	19.3	46.7	3.9
DMA	$1{,}8 \cdot 10^{-4}$	$3{,}2 \cdot 10^{-4}$	27.8	13.6	37.8	3.8
DMF	$4{,}1 \cdot 10^{-4}$	$6{,}6 \cdot 10^{-4}$	26.6	16.0	36.7	3.9
PDC	$2{,}7 \cdot 10^{-4}$	$2{,}9 \cdot 10^{-4}$	15.1	18.3	65.0	5.0
AN	$6{,}0 \cdot 10^{-5}$	$5{,}3 \cdot 10^{-5}$	14.1	19.3	36.0	4.0
NM	$3{,}7 \cdot 10^{-5}$	$2{,}2 \cdot 10^{-5}$	2.7	20.5	36.7	3.6
NB	$\ll 10^{-6}$		4.4	14.8	34.7	4.0

5. Conclusions

At present the term "association constant" is applied to entirely different equilibria involving different types of species, namely (1) to the union of free solvated ions, to give solvent-separated ion pairs, (2) outer-sphere complexes from free solvated ions, (3) unionized species from the free solvated ions and (4) unsolvated ion pairs from free unsolvated ions. The following terminology is based on experimental criteria and it has the advantage of allowing the correlation and rationalization of scientific facts in a logical system.
The term "ion pair" should be applied whenever the free ions retain their structural identity in ion-pairing processes. This is usually the case for solvent separated ion-pairs, but also in the limiting case of a "contact ion pair", e.g. the association of unsolvated (complex) ions, such as $[Bu_4N]^+[BPh_4]^-$.
By adopting these definitions the following reaction scheme is obtained:



It is apparent that the presented scheme is an attempt of an oversimplified systematization, in that it ignores the existence of an astonishingly great number of different species and equilibria in each system, which can be seen from the fact that the spectrum of relaxation times within a solution is widened by increase in solute concentration [56]. Despite these shortcomings this concept may serve the qualitative understanding and hence the re-interpretation of various experimental results. In addition many semiquantitative relationships are provided by applying the phenomenological parameters, which have been emphasized elsewhere.

It may appear strange that the question of the interpretation of the bonding forces involved in the different types of species and of interactions has not been raised. It is one of the great advantages of the extended donor-acceptor concept, that it can be applied to various types of molecular interactions [3], as it is solely based on phenomenological grounds and on measurable properties. There is no reason to raise this question as a prerequisite for a scientific discussion and indeed it is not required for the presented rationalization and visualization of hitherto unrelated phenomena.

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