Dynamics of solute-solvent interactions

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Abstract — This paper reviews some current concepts and recent experimental observations related to the way in which the simplest charged species, the electron and the proton, can interact with particular kinds of solvent molecules or aggregates. Electronic or protonic excess charges trapped on single molecules or shared by an aggregate of molecules can often preserve a high mobility, provided by particular mechanisms of structural diffusion.

The significant elementary events in the time course of the interaction of a solute with a dense, liquid environment are taking place on several different time scales. Not so very long ago we knew only the order of magnitude of these time scales. The duration of a collisional contact of molecules in a simple van der Waals liquid is of the order of $10^{-13}$ sec, the average time during which a pair of molecules remain neighbors is about $10^{-10}$ to $10^{-8}$ sec in solvents of ordinary viscosity. These values set only a frame of reference. The interesting questions arise when the dynamic behavior of particular solvents or particular solutes or their combinations becomes directly observable and reveals some aspects of their individuality.

Experimental methods for generating and recording very fast transient phenomena have evolved constantly in the last decades. Optical arrangements for producing picosecond and sub-picosecond laser pulses of any desired wavelength, as well as appropriate recording techniques for observing the temporal evolution of their photochemical effects, have been described. They are used to study intra- and intermolecular energy transfer, fluorescent or radiationless decay modes, rates of transition to and lifetimes of metastable triplet states, vibrational energy transfer, photodissociation, intermolecular energy dissipation and almost any other pathway for the diversion of the absorbed optical energy (ref. 1).

Relaxation rates of longitudinal and transverse magnetization in NMR experiments are another important source of knowledge about dynamic interactions in liquids and solutions. Determinations of the rates of exchange of acidic protons in aqueous media were among the early applications. Meanwhile pulsed NMR techniques have reached a state of considerable sophistication. Much of what is known about residence times of molecules in particular configurations, exchange rates of molecules in solvation shells, selective solvation in mixed solvents etc. has been obtained using the nuclear spin subsystem as a probe for sensing the molecular system from which it is part. Compared to NMR and other spectroscopic methods, neutron diffraction is one of the less accessible methods. Its resolving power for clarifying structural as well as dynamic aspects of molecular interactions in dense liquid phase is nevertheless remarkable. In non-magnetic media neutrons are scattered by elastic and inelastic collisions with atomic nuclei. The distribution of momentum transfers from and to thermal or subthermal neutrons, whose wavelength matches interatomic distances, can be measured with high precision in spatial direction as well as in energy. Pair correlation function in the hydration shell of ions as well as concentration dependent mobilities of bulk water and water molecules in the inner and outer layer of the hydration shell have been measured in this way (ref. 2).

A field that is traditionally rather remote from solution chemistry must be included here since it is beginning to yield an impressive amount of complementary information on interactions between isolated pairs or small aggregates of molecules. Instruments for generating beams of molecules and molecular clusters, mixing them with slow electrons or ionizing them by fast...
electrons, focusing, deflecting and sorting them according to their charge and mass, are becoming powerful tools for studying the properties of isolated, well defined states.

Last, not least, there is progress in theoretical and computational tools, although there still is a large gap between theory and experiment when dealing with the liquid state. Theory starts from microscopic models, often including extreme simplifications. The important theoretical parameters are not at all variable in an experiment, however, and therefore it is difficult to subject the theoretical hypotheses to significant experimental tests. Experiments observe the macroscopic reality. The distinctive features of different models become diffuse by the averaging needed to derive predictions about a measurable quantity.

The following sections will deal only with the dynamic behavior of two special solute species, namely excess and defect charges carried by solvent molecules. The dynamic phenomena that are of interest are of two kinds: 1. those directly associated with changes or transitions in the arrangement of solvent molecules in the field of interaction of a solute particle or aggregate of particles, 2. secondary effects on chemical transformations of dissolved entities.

**SOLVATED ELECTRONS**

Excess electrons are perhaps the simplest elementary particles that can easily be prepared and studied in vacuum. In liquid media the situation is quite different.

**Electrons in non-polar media**

In non-polar fluids, thermalized electrons are generated during energy deposition processes from ionizing radiation. Radiation induced conductivity in hydrocarbons was already measured very accurately in the beginning of this century (ref. 3). Electric mobilities can be measured even at very small and non-homogeneous concentrations. The surprising sensitivity of the excess electron mobility to the molecular shape of the solvent is borne out by the data (ref. 4) in Table 1. The activation energy of the radiation induced conductivity of solid low density polyethylene (ref. 5) has been included for comparison.

<table>
<thead>
<tr>
<th></th>
<th>$\mu$ (cm$^2$V$^{-1}$sec$^{-1}$)</th>
<th>$E_A$ (kJ mole$^{-1}$)</th>
<th>$V_0$ (kJ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neopentane (296 K)</td>
<td>55</td>
<td>&lt; 2</td>
<td>4.1</td>
</tr>
<tr>
<td>Neohexane (290 K)</td>
<td>12.6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane (329 K)</td>
<td>0.67</td>
<td>12</td>
<td>2.7</td>
</tr>
<tr>
<td>n-Hexane (307 K)</td>
<td>0.09</td>
<td>17</td>
<td>+ 0.4</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>33</td>
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The current view explains this behavior by assuming that the electron is periodically trapped by some localized structure in the solvent, and that it moves from trap to trap in a conduction band, separated from the highest occupied orbitals of the solvent molecules by an energy gap. The argument supporting this assumption comes from the observed temperatures dependence, which follows the exponential law $\mu = \mu_0 \exp(-E_A/RT)$, but without any correlation with viscosity or its energy of activation. $\mu_0$ is about 70 to 80 cm$^2$V$^{-1}$sec$^{-1}$ for all liquids in Table 1.

A lot of speculation is required to cast this view in a theoretical model that reveals something about the dynamics of the interaction of the excess electron with its environment.

Conduction bands are well understood for metals and semiconductors. In a crystal the wavefunctions of electrons are extended over many interatomic distances, in fact, in a perfect crystal the wavefunction for every electron extends over the whole crystal, with perfect coherence of the phase. Interferences between the periodicities of certain wavefunctions and the periodicity of the atomic lattice lead to singularities in their corresponding energies. Allowed and forbidden energy ranges appear if one classifies the stationary wavefunctions according to their energy.
In a fluid the periodicity of the lattice is only locally coherent, moreover, it fluctuates in time. The interference effects have only a restricted local range. The band structure of allowed and forbidden regions breaks up in local regions. In molecular fluids the molecular anisotropy increases the complexity of the fluctuating spatial pattern of allowed and forbidden regions for an electron of given energy.

The theoretical approach to describe phenomena associated with disordered localized structures with this bubble-like appearance is known under the appropriate name "percolation" theory.

An electron trapped in a localized region can move with it at the relatively low speed of the corresponding motion of the density fluctuation with which it is associated. From time to time it may escape by tunneling to neighboring regions. If it gains sufficient energy by inelastic phonon collisions, or by its interaction with the fluctuating electromagnetic fields, it may escape for a while to the extended region, until it is trapped again.

Hopping mechanisms between localized regions have been developed mostly in connection with the electrical properties of disordered or amorphous semiconductors. Percolation theory for jumping between randomly distributed localized regions does not, however, lead to the simple exponential dependence on 1/T but to exponential dependence on fractional powers of 1/T. For the one-dimensional case the predicted temperature dependence is \( \mu = \mu_0 \exp(-E_A/RT) \).

The experimental observation \( \mu = \mu_0 \exp(-E_A/RT) \) may be explained by a Boltzmann population equilibrium between two states with very different mobilities. In a given liquid the localized states must be of a more or less similar nature and have a similar energy distance to the mobile states. When the average residence time of the electron in each state is \( \tau_1 \) resp. \( \tau_e \), the mobility becomes

\[
\mu = \frac{\mu_1 \frac{\tau_1}{\tau_1 + \tau_e} + \mu_e \frac{\tau_e}{\tau_1 + \tau_e}}{\exp(-E_A/RT)}
\]

Experimental determinations of the rate of trapping (1/\( \tau_e \)) are not available for non-polar liquids. It is therefore difficult to decide whether the high-mobility state corresponds to the extended conduction band region or whether the high-mobility is effectively due to percolation hopping between localized regions (with a small temperature dependence). In this model the low-mobility state would be a particular local molecular arrangement, stabilized itself by the presence of the electron. When the excess charge is confined long enough within a local volume, the medium can yield to its repulsive, polarizing, electrostrictive and other interaction forces. In a crystal a slowly moving charge accompanied by the lattice deformation is called a polaron. The effective mass of the polaron is larger than that of the electron because the deformation requires displacement of the nuclear masses of the lattice. An electron may also be more permanently trapped in a lattice vacancy.

In a solid, the time needed to trap a "free" electron in the thermodynamically most stable "bound" polaron depends on the dielectric relaxation time and on the characteristic times of thermal energy exchange in the medium. The energy difference between the two states is of the order \( (\varepsilon_0^2/4\pi\varepsilon_\infty R)^*(1/n^2-1/\varepsilon) \), where \( \varepsilon_\infty \) is the optical and \( \varepsilon_\infty \) the static dielectric permittivity, and \( R \) is the effective radius of the polaron. In non-polar fluids \( n^2 \) and \( \varepsilon \) are not very different, hence the stabilization by polarization remains small.

Cavities or voids in the otherwise dense liquid structure also provide traps for localizing excess electrons. Due to coulombic repulsion between an excess electron and the electrons in molecular orbital clouds, the energy of the lower band edge of the conduction band \( V_0 \) is often positive with respect to the energy of the electron in vacuum or in the dilute gas phase, which we will set equal to zero as a reference value. Evidently, if the energy of lower edge of the conduction band in a dense medium is greater than in vacuum, localization of the excess charge in an evacuated cavity will lower to energy. The energy of the system containing a "free" electron can then be lowered by creating an internal cavity, in which the electron resides, if the sum of the surface and pressure work needed to create a cavity remains smaller than \( V_0 \). This work depends on surface tension \( \gamma \), pressure \( P \) and on the radius \( R \) of the cavity:

\[
4\pi R^2 \gamma + 4\pi R^3 P/3 < V_0
\]
Experimentally the energy of the quasi-free electron $V_0$ can be obtained from energy thresholds for adiabatic electron injection in the dense medium. The onset of the ionization continuum in the optical spectrum of dilute photol ionizable substances or photoelectric emission thresholds can be compared to their vacuum values. In the former case a correction for the energy of the polarization of the medium by the positively ionized absorber molecule must be made. Spectroscopic data for the liquid rare gases yield $V_0 > 0$ for He and Ne, and $V_0 < 0$ for Ar, Kr and Xe. There is reasonable agreement with theoretical estimates obtained with a simple model in which the macroscopic density and polarizability and the radius of an approximating hard-core repulsive potential are the only parameters (ref. 6).

For the liquids in Table 1 values of $V_0$ were obtained from measurements of the work function of metals in vacuum and in contact with the liquid (ref. 7). The increase in $V_0$ is much smaller than the increase in $E_A$. The same effect of molecular shape that increases the energy of the conduction band also seems to lower the energy of the trapped state. The spherical cavity model is too simple. The one-dimensional periodicity of chain-like molecules could have a larger influence on electron trapping in liquids than suspected so far. This is also suggested by the photoconductivity of certain classes of polymers.

In most polymers besides polyethylene, only a part of the excess electrons is "solvated" in relatively shallow traps of the order of up to several hundred millivolts under the free electron conduction band. Another part is bound to much deeper traps, from where they are released very slowly. Deep trapping may be a slow unimolecular process (cf. below). Polyethylene terephthalate must be doped with ca. $10^{-2}$ M trinitrofluorenone to reduce the radiation induced conductivity about 100-fold (ref. 8). The positive radicals resulting from X-ray photolization are usually considered not very mobile. The mobility of the defect electron in the valence band is not significant. Polytetrafluoroethylene and polyfluorethylenepropylene, however, are an example where hole conduction is considered to be dominant (ref. 9, 10).

Several unsaturated polymers (trans-polyacetylene, poly-p-phenylene etc.) show very high electrical conductivities (up to 1000 A V$^{-1}$ cm$^{-1}$) when they are doped with AsF$_5$ or some other good electron acceptors. Polyacetylene is a long chain of conjugated double bonds: $\cdots$ in which neutral radical states can nucleate by thermal activation: $\cdots$. When the unpaired electrons from the radicals are trapped by the dopant to form AsF$_5^+$, the remaining pair of positive holes can move as a bipolaron along the chain: $\cdots$. With very simple theoretical assumptions for the probability of pair transfer from one chain to a parallel neighboring chain, the experimentally found saturation effect of conductivity with dopant concentration the bipolaron model predicts the experimentally observed saturation effect of conductivity on dopant concentration (ref. 11).

Electrons in polar fluids

In liquid ammonia and a number of amines, ethers, more or less stable solvated electrons are produced when alkali metals are dissolved. The dissociation is primarily driven by the enthalpy of solvation of the metal cation, which easily exceeds the ionization energy of the metal. The stabilization of the electron that is liberated is very much affected by the free energy of solvation, for which one might expect in principle the same behavior (cavity formation) as in non-polar media, complemented by the electrostatic contribution of solvent polarization. This contribution should show the usual dependence on the dielectric constant and its temperature dependence, which usually leads to a negative entropy change that partly compensates the negative enthalpy change when an electric charge is immersed in a polar medium.

The thermodynamic properties of the solvated electron in liquid ammonia are now well established (ref. 12). On first view it is surprising that electron solvation in liquid ammonia is associated with a large positive entropy increase of the solute-solvent system. The entropy change associated with electron solvation at 233 K is 164 J mole$^{-1}$ K$^{-1}$.

On the other hand, the solvation entropies of other negative and positive ions are by at least 100 J mole$^{-1}$ K$^{-1}$ more negative in NH$_3$ than in H$_2$O at the same temperatures. It seems that the stability of the solvated electron in liquid NH$_3$ is for a very large part contributed by a structural effect that translates itself in this large entropy gain. In most theoretical models entropic contributions have not been explicitly considered. From an
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early theoretical model with 4 hard-core dipolar molecules, arranged around a cavity of 1.7 Å radius (this loose packing leads to an effective cavity radius of 3.1 Å for the volume occupied by the electron), the experimental volume and enthalpy change and the main features of the optical properties could be derived (ref. 13). A more recent numerical Monte Carlo calculation (ref. 14), in which the electron is represented by a dynamic random closed path in between and around several moving solvent molecules in a simulated fluid, concluded that the coordination number (number of NH₃ molecules in the most inner solvation shell) is about the same for a classical anion as for a solvated electron and of the order of about 8 to 9. The pair correlation functions for the atom distributions around the center of mass of the solvation structure are much less sharply peaked for an electron as compared to the ion. For the H-atoms a peak corresponding to the second solvation shell is almost absent, and even for the first nine inner solvating molecules the H-atom distribution is very diffuse. In these calculations rigid solvent molecules with fixed fractional charges on the H- and N-atoms were assumed. The predicted optical excitation energy is still twice as large as the experimental value, indicating that the compact charge density, with a diameter of about 4 Å, derived from these calculations is still too dense.

Pair correlation functions for the distance distribution between the electron and the fractional charge sites on the NH₃ molecules show that the excess electron density around the positive charge sites decays in a way similar to that in a hydrogen-like atom with a fractionally charged nucleus, while it avoids the negative sites on the nitrogen atom.

These results make it easier to understand the positive entropy of solvation of the electron as a quantum particle. Its wave-like nature allows it to interact simultaneously with the individual (fractional) charge-carrying sites on the solvent molecules. The mutual electrostatic interactions between solvent molecules become thereby shielded. The configurational constraints and mutually enforced correlations of movements are reduced.

In contrast to an ion, the electron does not "polarize" the dielectric environment in liquid NH₃, but rather "depolarizes" the existing mutual interactions in the solvent.

The large positive entropy of solvation is lost when the electron is transformed into a bound electron, localized in an atomic or molecular orbital. This is the case in reactions like

\[ e^- + \text{NH}_3 \rightarrow \frac{1}{2} \text{H}_2 + \text{NH}_2^- \]

which is not observed although it is thermodynamically favorable. It is kinetically hindered because the intermediate formation of H-atoms

\[ e^- + \text{NH}_3 \rightarrow \text{H} + \text{NH}_2^-; \quad \Delta H^0 = 125 \text{ kJ mole}^{-1}; \quad \Delta S^0 = -272 \text{ J K}^{-1}\text{mole}^{-1} \quad (1) \]

is extremely unfavorable, and the direct bimolecular process

\[ 2e^- + 2\text{NH}_3 \rightarrow \text{H}_2 + 2\text{NH}_2^- \]

\[ \Delta H^0 = -168 \text{ kJ mole}^{-1}; \quad \Delta S^0 = -466 \text{ J K}^{-1}\text{mole}^{-1} \quad (2) \]

is too slow due to the large entropy loss in the transition state. It must also overcome a coulombic activation barrier for bringing together two electrons in the same solvation shell. Electron dimers exist in more concentrated metal solutions in liquid NH₃, but they are associated with a metal cation.

In H₂O hydrogen formation takes place rather rapidly, however, and rate constants have been assigned to each of the corresponding processes:

\[ e^- + \text{H}_2\text{O} \rightarrow \text{H} + \text{OH}^- \quad (3) \]

\[ 2e^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^- \quad (4) \]

The rate constant of reaction (3), \( k_3 \approx 10^3 \text{ sec}^{-1} \), is inferred from the transient absorption decay of electrons generated in very small concentrations by hard-UV flash photolysis of alkaline solutions (OH⁻ → OH+e⁻). Under these conditions the competing process \( e^-+\text{H}_2\text{O}^+ \rightarrow \text{H}+\text{H}_2\text{O} \) is excluded. The electron concentration is too small (\( c_e \approx 10^{-7} \text{ M} \)) for competition from
the bimolecular process, which becomes dominant, however, in pulse radiolysis experiments where much higher concentrations can be obtained.

Doubts have been expressed about the assignment of the observed unimolecular decay (ref. 15). It has not been shown convincingly that the decay of the electron produces H and OH\(^+\), corresponding to reaction (3). Instead, the decay leads to an intermediate with an absorption maximum at 270 nm, from which the hydrated electron can be photochemically recovered. The intermediate then decays in a bimolecular process which seems to be nearly diffusion controlled.

If the rate constant assigned to reaction (3) belongs to a different process, the presently accepted value for the entropy of solvation of the electron in \(\text{H}_2\text{O}\) may have to be revised. The present value \(S_{\text{aq}}^0 = 8 \text{ J K}^{-1}\text{mole}^{-1}\) was obtained with the equilibrium constant of reaction (3), which is determined kinetically by the ratio of forward and backward rate constants. The backward rate constant, \(k_{-2} = 2\times10^7 \text{ M}^{-1}\text{sec}^{-1}\), follows from direct measurement of the appearance rate of solvated electrons when hydrogen atoms are injected in alkaline \(\text{H}_2\text{O}\). A forward rate constant much smaller than the presently attributed value would imply a more stable hydrated electron and therefore a lowering of its enthalpy or an increase in its entropy.

The presently accepted value for the entropy of hydration of the electron in \(\text{H}_2\text{O}\) is still more positive than that of other ions, but the difference is much smaller than in \(\text{NH}_3\). What could make the water structure more resistant to structure breaking? An obvious reason is that the structure is much stronger, as indicated by the difference in boiling points and heats of vaporization. In \(\text{NH}_3\) the maximum number of hydrogen bonds that can be formed is one per molecule, in \(\text{H}_2\text{O}\) this number is twice as large, moreover, bond energies are larger. Probably the open water structure does not need very much rearrangement to provide room for a trapped electron.

The rate constants for unimolecular decay of solvated electrons produced by pulse radiolysis in aliphatic alcohols are one to two orders of magnitude larger than for \(\text{H}_2\text{O}\) (ref. 16). The reaction may be similar to reaction (3). Then the faster rate would indicate that alkyl radicals instead of H-atoms are produced. Several alternatives exist, of course. In methanol and ethanol the unimolecular decay time constant is 10 microseconds. The lifetime in propanol to nonanol is twice as long, and independent of the length of the aliphatic chain.

Electrons solvated in clusters of \(\text{H}_2\text{O}\) or \(\text{NH}_3\) molecules have been prepared by mixing a rapidly expanding high density gas jet with low energy electrons, emitted photoelectrically from a UV-illuminated filament in the vicinity of the adiabatically expanding beam. By mass spectrometric analysis the distribution of \((\text{H}_2\text{O})_n^+\) with \(11 < n < 50\) or \((\text{NH}_3)_m^-\) with \(36 < m < 100\) is determined. \(\text{CH}_3\text{OH}\) or \(\text{C}_2\text{H}_5\text{OH}\) clusters of this kind could not be prepared so far (ref. 17).

Cluster formation and electron trapping takes place when the gas is super-saturated by adiabatic cooling. It is probable that the electron is trapped by already preformed neutral clusters. Electron solvating clusters with less than 11 \(\text{H}_2\text{O}\) resp. 36 \(\text{NH}_3\) molecules are not found, although neutral clusters of smaller size are definitely present in the expanding beam.

The rate of free electron trapping by \(\text{H}_2\text{O}\) was recently studied using subpicosecond photonization of phenothiazine incorporated in micelles (ref. 18). The electron produced inside a micelle, formed by surfactant molecules in aqueous solution, moves to the aqueous phase where it is trapped. With sodium lauryl sulfate as the surfactant molecule, the whole process takes less than half a picosecond. A dependence on the nature of the surfactant was observed, however, suggesting that the rate determining step might be related to electron migration rather than to its hydration. This is confirmed when the same experiment is carried out with inverted micelles. Inverted (or reversed) micelles are small water pockets, solubilized in a nonpolar solvent by surfactant molecules. The size of the pocket depends on the molar ratio \(\text{H}_2\text{O}/\text{surfactant}\) used in the preparation. In inverted micelles prepared with Aerosol-OT (sodium bis-2-ethylhexylsulfosuccinate) the hydration of the electron occurs with a time constant of at most 100 femtoseconds.

In earlier measurements (ref. 19) picosecond photonization of \(\text{Fe(CN)}_6^{3-}\) in aqueous solution did show a much longer time lag for the appearance of the absorption band of the solvated electron. The long wavelength part of
the absorption developed with a time constant of about 2 psec, the full absorption band develops from longer to shorter wavelength in about 4 psec.

Whereas a formation time of 0.1 psec excludes a structural rearrangement, the characteristic time of 2 to 4 psec is of the order of the viscoelastic relaxation time of 1.4 psec obtained from ultrasound absorption, the molecular orientational correlation time of 2.5 psec found from NMR, and the dielectric relaxation time of 10 psec.

**SOLVATED EXCESS AND DEFECT PROTONS**

Can the notion of a solvated electron as an excess charge, distributed over a cluster of solvent molecules, also be applied to the solvated proton and defect proton that play such an eminent role in the chemistry of acids and bases? And is this valid for the corresponding wave- length difference of the electron and the proton as quantum particles, as compared to their charge ratio? In solvents there can be a distribution of the excess charge, contributed by a solvated excess proton over the solvation structure. In hydrogen bonds fast dynamic bond length changes of a bound proton can occur. For phenomena related to the dynamic displacements of the excess proton over larger distances, however, the accompanying mass dispacements cannot be ignored. There is no bandgap and extended conduction band for the proton. Besides the normal mode of diffusive transport of a solvated ionic charge, where the charge remains associated with the same atomic nucleus and even with the same molecules of the solvation shell, some solvents can provide a dynamic solvation environment in which this association is broken.

The simplest "distributed" excess proton seems to be in the H₃⁺ ion, which is formed by photoionization or electron impact ionization of H₂ in the reaction H²⁺ + H → H₃⁺. In H₃⁺ the nuclei form an equilateral triangle (ref. 20, 21). H₃⁺ is probably the most important "acid" in interstellar space, where H₂ is the most abundant species. H₃⁺ is constantly generated by cosmic ray ionization, but looses a proton to other species to form CH⁺, NH⁺, etc. These then react further with H₂ in bimolecular hydrogen abstractions reactions AH⁺ + H₂ → AH⁺H₂⁺ + H until they are saturated or neutralized by electrons AH⁺H₂⁺ + e⁻ → AH⁺ + H. On collision, a free proton and a neutral particle, both with low thermal energy, may combine to a more stable charged polyatomic ion. Even rare gas atoms share their electrons with a proton to form species like HeH⁺, whereas negatively charged ions like He⁻ or Ne⁻ would immediately dissociate into a free electron and a neutral atom.

Contrary to the electron, for which the strong repulsive forces due to the Pauli exclusion principle compel it to compete for free space in a dense medium, until it finds a stable place in a vacant atomic or molecular orbital, the proton is likely to bind to a hosting molecule by polarizing and penetrating the electron shell. The excess proton is thus engaged in a true chemical bond with its carrier molecule. Energetically such a bond can be very stable, e.g. in NH₃⁺, which is another example of a "distributed" excess proton.

Two questions arise: 1) Can an excess proton bind simultaneously to more than one host molecule? 2) What determines the dynamic stability of the charged host complex with respect to the exchange of one host molecule for another, identical or different one?

**Gas phase acid-base chemistry**

For a large number of substances the proton affinities (enthalpy decrease by proton attachment, PA = -ΔHº) have been determined in the gas phase (ref. 22). Size (polarizability), unsaturation (rehybridization) and charge spreading ability by the host molecule are directly reflected by this quantity.

The attachment of an excess proton in general labilizes the chemical bonds to the hydrogens already in the molecule. Intramolecular proton exchanges in substituted biphenyl cations have been studied using deuterium substitution, showing that even between the two rings interconversion is occurring rather rapidly (ref. 23).
In the gas phase proton exchange between different host molecules occurs within a single collision only when the free energy decreases by a rather large amount, usually at least 25 kJ mole⁻¹. Quasi-unimolecular reaction rate theory (RRKM—theory) has been invoked to explain the activation requirements of some of the proton exchange reactions, assuming that a weakly H-bonded intermediate with a double potential well is formed (ref. 24).

The formation of hydrogen-bonded dimers, dimeric complexes and clusters containing an excess proton is now studied for an increasing number of compounds. For many complexes the dissociation enthalpies are linearly related to the difference in proton affinities of the partners, leading to the empirical relation ΔH_diss = const - (0.5±0.04)ΔPA, which is found to hold (ref. 25) over a ΔPA range from 0 to 300 kJ mole⁻¹. In clusters of the type BH⁺(H₂O)_n, with n = 1 to 4, the enthalpy ratios for consecutive hydrations turn out to be rather independent on the nature of the BH⁺ for simple structures. Thus the amount of charge-transfers in the first hydrogen bond seems to be transmitted partly and in constant proportion to the next three hydrating H₂O molecules.

It is evident that our knowledge on the thermodynamic stability of small molecular aggregates containing excess or defect electrons or protons is expanding very rapidly. The combination of these new preparative and analytical techniques with high-resolution molecular spectroscopy, as it is now available using fine-tuneable laser sources, will add the structural information that is required to calculate the entropic contributions. We therefore can expect a considerable improvement in our understanding of solvent effects on acid-base processes when the isolated phenomena in the gas phase become available as a standard for comparison.

**ACID–BASE REACTIONS IN POLAR SOLVENTS**

Solvent effects on acid-base reactions have been mainly studied by comparing relative equilibrium shifts, for setting up pH scales in various media. The kinetics of many acid-base processes in aqueous media have been studied, mainly with chemical relaxation methods. A coherent picture of the dynamic factors has emerged. The reaction mechanism can be classified in 3 types:

a) The recombination of a water-solvated proton (for simplicity usually written as H₃O⁺) with a base, or of a water-solvated defect proton (OH⁻) with an acid, is a diffusion controlled process if the proton-accepting atom of the base or proton-releasing atom of the acid are participating in the hydrogen bond structure of the solvent.

b) If these atoms do not qualify for easy H-bond formation with the solvent, e.g. for the majority of carbon acids, or where large electron delocalization is more favorable than local bond formation with the solvent, then the rate of incorporation in the hydrogen bond structure becomes rate limiting. Usually this rate depends on the pK-difference of the reacting species but the reactions are not diffusion controlled.

c) When the proton in an acid is involved in an intramolecular hydrogen bond, the population pre-equilibrium between intramolecular and intermolecular (solvent-) hydrogen-bonded species determines the rate of transformation (ref. 26).

This does not only hold for water-solvated H₃O⁺ or OH⁻, but also for mutual proton exchanges between acids and bases when the pKₐ of the protonating acid is lower than that of the protonated base. The solvent participates in the exchange of the proton when the reaction is diffusion controlled. One should remember that a diffusion limited process in the forward direction always implies a diffusion controlled backward reaction, preceded by the reaction equilibrium, in an equilibrium system (microscopic reversibility). The slow reverse reaction of a diffusion controlled forward reaction gives no information about the rate of different transformation steps inside the encounter complex.

Participation of the solvent is not always possible in non-aqueous media. In this case the formation of the encounter complex is not necessarily the rate limiting step.

Kinetic studies of prototype reactions involving phenols as acids have been carried out recently in N-methylformamide (ref. 27) and in benzonitrile.
The first solvent is a very weak acid and a very weak base in aqueous medium. In the pure liquid it shows autodissociation, leading to an ionic product (autoprotolysis constant) exceeding that of \( \text{H}_2\text{O} \) by orders of magnitude. The autoprotolysis constant can only be explained by the formation of stable, probably dimeric, solvation structures for an excess proton. Compared to the stabilities of the protonated, \( \text{H}_2\text{O} \)-solvated N-methylformamide cation and its deprotonated \( \text{H}_2\text{O} \)-solvated anion in water, the large autoprotolysis constant can only be explained by the formation of stable, probably dimeric, solvation structures for an excess proton.

The low free energy of an excess proton localized in a strong homonuclear hydrogen bond between two solvent molecules in this case causes a sizable activation energy for the exchange of one of the solvating host molecules by another one, or by a proton accepting base. This is probably characteristic of acid-base reactions in polar solvents that have a strong hydrogen bond acceptor site on an atom that is not hydrogenated. Many amides, ketones, ethers, esters, phosphine oxides, tertiary amines, pyridines, and other compounds belong to this class.

In aprotic polar solvents with weak, delocalized hydrogen bond acceptor sites like chlorobenzene, nitriles, nitro-compounds, the activation steps are more of a steric nature. In such media of self-associated structures like \( \text{H}_2\text{O} \)-dimer etc. are often found (ref. 28,29).

In water, alcohols, primary and secondary amines as well as certain symmetrically built molecular structures like carboxylic acids, imidazoles, a multiple proton exchange mechanism is possible, assisting the fast transposition of a proton from one place to another. This motion is associated with a change in orientation of the molecular conformation and its electrical dipole orientation. The full electrical charge of the displaced proton is not completely transferred by such a multiple exchange. The preceding reorientation of the intervening molecules and their dipole field is part of the full charge (and mass) transfer. The mechanism nevertheless provides essentially a decoupling of the motion of a proton and is associated with the translational motion of the other atoms of the solvating structure. A proton that is tightly locked in an intramolecular \( \text{H} \)-bond, or solvated in a single homonuclear \( \text{H} \)-bond between two solvent molecules, can only move as fast as its surrounding molecular environment.

Some ambifunctional molecules, carrying an \( \text{H} \)-bond donor and an acceptor on different atoms, can still facilitate some proton displacements by undergoing an isomerization, e.g. by the formation of a Schiff's base in the case of N-methylformamide. The free energy change for the transformation must then be compensated by that of the facilitated acid-base equilibrium.

The multiple exchange mechanism for moving protons through a hydrogen-bonded liquid is responsible for the high value of the mobility of solvated protons and hydroxyl ions in water; the difference between charge densities of such protons and that of other monoatomic cations like \( \text{Na}^+ \), \( \text{K}^+ \), has sometimes been named "extra-mobility". This term should not be used to describe the fast displacement of one or more protons in an existing chain of hydrogen bonds, because this is only a part of the complete translocation of the protonic charge and mass. The rates of individual steps (bond formation and breaking, reorientation of the OH, lone pair and dipole direction on an oxygen atom, proton transfer between oxygen atoms) are not easily accessible for measurement. A theoretical treatment for making a sufficiently realistic computational simulation of the dynamics of such a system possible is not available. The dynamic behavior of the proton in its hydration shell remains a favorite object of discussion among the many other properties that make water an exceptional substance. In a series of papers H.G. Hertz critically re-examined (ref. 30) three of the most directly observable dynamic properties of pure liquid water caused or influenced by the presence of excess and defect protons: electrical conductivity, self-diffusion coefficient, and NMR line shape. In an effort not to depend on additional information from measurements in more concentrated acid or base solutions, it is shown how the concentration of charge carriers can be estimated from every pair of these observable quantities. This requires, of course, a minimal assumption about the identity of the charge carriers. Once such an assumption is made, and further sources of information on the behavior of the system (e.g. reaction rates, solution conductivities, structural information from IR-spectra, neutron diffraction etc.) are ignored, it is evidently not possible to derive more details about the mechanism. Such information is not available, but putting together a tractable, fine-grained, theoretical model that reflects both the structural and dynamic properties of liquid \( \text{H}_2\text{O} \) will probably remain a challenge for many years.
The interactions between a solute foreign ion or molecule and its immediate neighboring contact partners can often be investigated with specific chemical or spectroscopic techniques. Long range effects on the solvent remain still controversial. Solutes have been classified as structure-making, structure-breaking, mostly without a clear definition of the microscopic properties of the postulated structure. When the mutual interactions between solvent molecules are stronger than those with a solute, there will be a tendency to keep the solvent packing structure intact and to force the solute molecules together in dimers or higher aggregates, even if the solute molecules have no affinity whatsoever for each other. This general "solvophobic" interaction is modified by the possible interactions between the solute molecules (mutual orientation, stacking etc.).

The creation of cavities in the packing structure of a solvent requires a repartition of their mutual arrangements. In hydrogen bonded media like H₂O, the rearrangement and the change in available hydrogen bond acceptor and donor sites influences the mechanism of proton transport. The effect of dissolved salts on the proton exchange rate of water appears in the line shape of ¹H NMR spectra (ref. 31). Ions known as structure breakers (NaClO₄, KI) slow down the rate of exchange by a factor of 10 in very high concentration. Structure formers should increase the exchange rate. This is indeed the case for MgCl₂ and LiCl₂. Tetraalkylammonium salts, supposed to be structure formers by other criteria, behave as structure breakers.

REFERENCES