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Structure and dynamics of non-aqueous solutions

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Abstract. The structure and dynamics of non-aqueous solutions are discussed. Specific properties of these solvents are investigated, especially by neutron scattering experiments, and details are given of their technological applications.

1. Introduction

The physics and chemistry of non-aqueous electrolyte solutions are relevant to fundamental research and industrial applications. A convenient choice of the solvent can help us to study effects which cannot be separated in aqueous solutions. The chemical and thermal stability of non-aqueous electrolyte solutions are important features in many technological applications. For many ions water is too reactive. For example a lithium battery would not be possible in aqueous media. The wide range of the properties of organic solvents leads to a great flexibility in the design of systems. Some frequently used solvents are given in table 1.

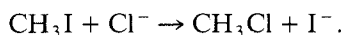
The classification of solvents is based on their acid-base properties which is a general measure of their ability to react chemically with other species. For example, acetonitrile is a protophobic solvent that solvates poorly inorganic cations. This is in contrast to DMF which is protophilic and solvates inorganic cations well.

2. Application and technological interest

Among the considerable number of applications which non-aqueous solutions have found until now, four examples are arbitrarily selected here. The examples are taken from [1] where a large number of technological applications are discussed in detail.

2.1. Chemical reaction in organic solvents

(i) *Kinetic salt effects.* It is well known in organic chemistry that the kinetics of reactions depends strongly on the choice of the solvent. An example is the nucleophilic substitution of iodide in CH_3I by a chloride ion:



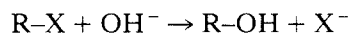
Changing the solvent from methanol to acetonitrile or DMF causes the rate constants to

Table 1. Classification of solvents according to their acid-base properties [1]. Θ_F , fusing point; Θ_B , boiling point; ϵ , dielectric constant; η , viscosity at 25 °C.

Solvent class	Example	Θ_F (°C)	Θ_B (°C)	ϵ	η/cP
	Protic solvents				
Amphiprotic hydroxylic	Water				
	Methanol	-98	65	33	0.54
Amphiprotic protogenic	Acetic acid	17	118	6	1.13
Protophilic H-bond donor	Formamide	3	218	109	3.30
	Aprotic solvents				
Aprotic protophilic	Dimethylformamide (DMF)	-60	153	37	0.79
Aprotic protophobic	Acetonitrile	-49	82	36	0.34
	Propylene carbonate (PC)	-55	242	65	2.51
Low permittivity electron donor	Diethylether	-116	35	4	0.24
Inert	Cyclohexane	7	81	2	0.90

increase by several orders of magnitude although the dielectric constants are similar. This is due to a drastic decrease of anion solvation from methanol to acetonitrile and even more to DMF.

(ii) *Phase-transfer reactions.* Phase-transfer of ions from the aqueous to an organic phase is desirable for poorly soluble reactants. An example is the hydrolysis of alkyl halogenides:



R is a general organic group, X the leaving halogenide. Typical phase transfer catalysts are tetraalkylammonium salts. Their cations are soluble in the organic solvent and exchange their counterions with the ions in the aqueous phase. Even when only a small amount of OH^- ions is dissolved in the organic phase, these ions will react immediately with the organic co-reactant provided that they are neither highly associated with the tetraalkylammonium ions nor highly solvated by the organic solvent. If the reaction is fast enough other OH^- ions are permanently delivered from the aqueous phase.

2.2. Electrodeposition

In some cases the electrodeposition of metals from aqueous solutions is not possible because hydrogen evolution occurs instead of metal deposition. Another method, fused salt electrolysis, is very expensive because it uses high temperatures which require high energies. Non-aqueous solutions are an alternative. An example of a commercial application is in the electrodeposition of aluminium from a solution of $LiAlH_4$, $AlCl_3$, and anhydrous diethylether.

2.3. High-energy batteries

Batteries based on non-aqueous electrolyte solutions reached the level of commercialization about twenty years ago. These non-rechargeable primary batteries work essentially with lithium as the anodic material in different solutions. An example is the $Li/LiClO_4$ (propylene carbonate)/ Ag_2CrO_4 cell used in pacemakers. Other frequently used solvents are DME, acetonitrile or SO_2 .

The important parameters are high specific conductance of the solution ($>5 \times 10^{-3} \text{ S cm}^{-1}$), high mobility of the active ion, a large temperature range ($-50 \text{ }^\circ\text{C}$ to $50 \text{ }^\circ\text{C}$), sufficiently high solubility of the electrolyte compound ($>0.3 \text{ mol dm}^{-3}$) at all temperatures and compatibility with the lithium anode and the cathode.

3. Structure and thermodynamics of non-aqueous solutions

The discussion of the structure of solutions is mainly concerned with the solvation or association of the dissolved ions. From a more chemical point of view it involves defining ion pairs, triples, complexes, and ligands or more physically use is made of statistical mechanics correlation functions. Both chemical and physical models are tested by comparison with experimental results.

In the simplest case these experiments yield thermodynamic data such as osmotic coefficients. But even these classical experimental methods turn out to be very difficult when applied to non-aqueous solutions. The reason is that very pure solvents and solutes are required for good experimental results. Sometimes new methods of solvent purification have to be developed.

Further problems arise when methods based on aqueous standards cannot be transferred to non-aqueous solutions. An example is the isopiestic method frequently used for aqueous solutions in order to determine osmotic coefficients. Nearly ten years ago a new apparatus was constructed for absolute vapour pressure measurements on non-aqueous solutions. With this equipment osmotic coefficients of a variety of solutions in different solvents were determined with high precision [2].

In contrast to thermodynamic data yielding only integrals over ionic distributions, scattering experiments yield a more direct picture of the solution. The results are given in terms of time-averaged $g(r)$ or time-dependent $g(r, t)$ correlation functions which play a central role in statistical mechanics.

Neutron diffraction arises from the interaction of an incident beam of neutrons and the nuclei of the scattering probe. The measured neutron intensity is a function of the angle Θ and the wavelength λ of the neutron beam. These quantities yield the so-called wave number transfer q , $q = (4\pi/\lambda) \sin(\Theta/2)$.

If only the time averaged structure of the solution is required, neutron intensity is recorded as a function of q , due to scattering of all particles in the solution. The spectrum depends on the nature of the atoms in the solution, the size and the shape of the particles and the correlations between the particles. The dynamical behaviour of the particles is obtained measuring the intensity of the scattered neutrons as a function of their energy.

We performed two types of neutron scattering experiments on non-aqueous solutions recently in order to measure ion-ion ('association') and ion-solvent ('solvation') interactions.

3.1. Small angle neutron scattering (SANS) on tetraalkylammonium salt solutions in deuterated solvents

SANS measurements cover a q range from 2×10^{-3} to at most $1 \text{ } \text{\AA}^{-1}$, corresponding to a resolution of about $6 \text{ } \text{\AA}$ [3–5]. In this region the contribution of the solvent is almost independent of the angle and, when deuterated, its absolute intensity is small. It can be measured separately and subtracted from the solution spectrum. The remaining intensity is due to coherent and incoherent scattering of the electrolyte which can be split by

convenient equipment or calculations. The comparison of the measured intensities with standards (e.g. water) allows the coherent scattering contribution of the ions on an absolute scale to take place.

As a consequence of a resolution of about 6 Å, the measurements cannot reflect molecular details smaller than this value. The solvent can be considered as a continuous medium of constant scattering density s_0 and ions as particles with suitable volumes and shapes and also with uniform scattering densities, $s_i = b_i/v_i$ where b_i is the scattering length of a particle of type i . v_i is its partial molecular volume. The scattering lengths are characteristic constants known for the atoms, the molecular volumes are determined by density measurements.

Under these conditions the McMillan–Mayer level of description is a theoretical analogue of the experiment. The interactions of the ions are described by solvent-averaged ion pair potentials of spherical symmetry. The coherent intensity of neutrons scattered from the ions, $I^{\text{coh}}(q)$ is

$$I^{\text{coh}}(q) = \sum_{i=1}^2 \sum_{j=1}^2 (s_i - s_0)v_i(s_j - s_0)v_j F_i(q)F_j(q)S_{ij}(q)$$

where

$$F_i(q) = 3(\sin(qa_i) - qa_i \cos(qa_i))/(qa_i)^3$$

is the form factor of a spherical ion i of radius a_i . $S_{ij}(q)$ is the structure factor

$$S_{ij}(q) = \rho_i \delta_{ij} + \rho_i \rho_j \frac{4\pi}{q} \int_0^\infty \sin qr [g_{ij}(r) - 1] r dr.$$

ρ_i is the number density of ion i , and δ_{ij} is Kronecker's symbol. The ion pair correlation functions $g_{ij}(r)$ can be calculated by integral equation techniques like the 'primitive model' HNC. However, it is well known that HNC is not always a good approximation for low permittivity solutions. Therefore we carried out a Brownian dynamics (BD) simulation in which we used the same solvent-averaged potentials. In this way the reliability of the HNC calculations was verified.

Up to now two solutions have been studied as a function of concentration: n-tetrapentylammonium bromide (Pe_4NBr) in deuterated acetonitrile and in deuterated 2-propanol. For these systems it can be inferred that the chains of the cations are almost completely stretched and that cations can penetrate into other cations up to nearly the first carbon atom surrounding the nitrogen one. There is no maximum in the $g_{++}(r)$ function which has a value significantly higher than one.

The coherent intensity extrapolated to the wave number transfer $q = 0$ corresponds to the thermodynamic limit. Consequently, it can be related to the osmotic coefficient φ of the solution

$$I^{\text{coh}}(q = 0) = \{[(b_1 + b_2)/(v_1 + v_2) - s_0](v_1 + v_2)\}^2 S(0)$$

with

$$S(0) = N_A c \frac{\partial c}{\partial c \varphi} 1000$$

where N_A is Avogadro's number and c is the salt concentration in mol l^{-1} . I^{coh} is given in cm^{-1} . The osmotic coefficients of this particular system have been recently

determined. A comparison between measured $I^{\text{coh}}(0)$ and those calculated from osmotic coefficients gives a hint at the precision of the measurements. It also explains that $I(0)$ can decrease when salt concentrations are increased up to high values. Details are given in a separate paper [5].

3.2. Large angle neutron scattering (LANS) on a lithium salt in deuterated acetonitrile

The resolution of the experiment depends on the q range studied [6, 7]. Taking a large q range up to 16 \AA^{-1} (angular range $0\text{--}128^\circ$, $\lambda = 0.712 \text{ \AA}$) gives a detailed picture of the solution down to particle distances as small as the diameters of small alkali ions. Following Enderby and co-workers [8] two samples are studied which are identical in all respects except for the isotopic state of the lithium ion in a 0.58 M solution of LiBr in acetonitrile. The difference between the two scattering functions eliminates distortions due to inelastic effects. Furthermore, all correlations are suppressed which do not concern the lithium ion. In this way we obtained atom–atom correlations between the lithium ion and either the bromide counterion or an atom of the acetonitrile molecule.

The evaluation of the data shows that the lithium ion has a tetrahedral environment created by three acetonitrile molecules and one bromide ion. The lithium–bromide interaction can be interpreted as a high association. A chemical model based on thermodynamic data yields a value of 143 kg mol^{-1} for the association constant K_α . The result supports the picture of bad solvation of inorganic cations and inorganic anions with localized charges. The counterion can easily penetrate into the first solvation shell. The resulting ion pairs behave like neutral particles. Hartree–Fock calculations on isolated LiBr atoms or clusters with an acetonitrile solvation shell confirm the surprisingly small distance Li–Br of closest approach: it is about 2 \AA . The peak in the correlation function has a maximum near 2.45 \AA .

In contrast, an analogous experiment in an aqueous LiBr solution shows that the tetrahedral environment contains four water molecules and no counterion.

Details will be given elsewhere [6, 7].

4. Structure and dynamics of non-aqueous solutions

The mobility of the solute particles is of great interest for technical application. It also yields information about the structure of the solution since association or solvation will strongly influence transport properties. In this regard conductance measurements on dilute and concentrated solutions yield a wealth of information on ion pairing and formation of higher aggregates [1]. A great drawback is the lack of reliable transport theories beyond the limiting laws. Therefore we recently followed another strategy [9, 10]. We correlated the results of quasielastic neutron scattering (QENS), NMR spin echo, SANS, and vapour pressure measurements with the help of HNC and BD calculations. The system under consideration was Pe_4NBr in deuterated acetonitrile.

For QENS measurements detectors are placed at various values of q around the sample, and for each q the number of scattered neutrons is counted as a function of their energy ω . The measurable incoherent neutron scattering intensity $I^{\text{incoh}}(q, \omega)$ arising from the cations is related to the Fourier transform $S^s(q, \omega)$ of the time dependent cation correlation function $g_+^s(r, t)$. $I^{\text{incoh}}(q, \omega)$ is calculable by simulation techniques. In the

quasielastic region $I^{\text{incoh}}(q, \omega)$ is reproduced by models which take rotational and translational diffusion into account. The model for the translational diffusion allows us to infer a cation self-diffusion coefficient D^+ .

Since the QENS technique works in the picosecond time scale, the self-diffusion coefficient reflects only hydrodynamic interactions which can become important in a solvent of low viscosity η (see table 1) [11]. The NMR technique which works in the millisecond time scale, yields a significantly different self-diffusion coefficient because D_{NMR}^+ also comprises the relaxation contribution of the ionic cloud [10].

The difference $D_{\text{NMR}}^+ - D_{\text{QENS}}^+$ was approached by a BD simulation using a convenient solvent-averaged potential without hydrodynamic interactions [9]. The diffusion coefficient is mostly influenced by cation–anion interaction whereas small-angle neutron scattering of tetraalkylammonium halide solutions yields especially information about cation–cation interactions. Furthermore the osmotic coefficients are related to the integral over all three ion–ion correlation functions. HNC calculations and BD simulations allowed us to infer ion–ion correlation functions which are in agreement with the experimental results. It was found that the bromide ion penetrates slightly into the cation chains. The peak maximum of the $g_{+-}(r)$ function is near 10 \AA . The overall cation–anion association is small ($K_{\alpha} \sim 8 \text{ kg mol}^{-1}$ [12]). The small association and small solvation of bromide ions in acetonitrile (cf section 3.2) are in agreement with the requirements of phase-transfer catalysts, cf section 2.

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