

Structuring at solid interfaces in binary solvent mixtures

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Abstract

The presence of a charged solid interface within a solvent mixture can induce locally and also at some distance from the interface a wealth of changes: in composition; in molecular ordering and orientation; in preferential ion solvation. This paper presents both a rewarding multinuclear magnetic resonance methodology and some of the most interesting results it provides.

INTRODUCTION

When a solid of any shape is dipped into a liquid, the molecules of the fluid have their motion restricted to those portions of space unoccupied by the solid. Furthermore, their collisions with the solid differ, for instance in stickiness, from their intermolecular collisions. Beyond such rather trite but true assertions, we have concerned ourselves with the topic of solvent organization, reorganization and disorganization in the vicinity of a solid interface with a view to gain insight into an important factor in heterogeneous catalysis.

Indeed, we were able to show recently that a spectacular case of substrate selectivity, so incredibly efficient as to evoke enzymatic action, was due to such factors. More precisely, a combination of chemisorption as the rate-determining step and of preferential occupation of the catalytic sites by only one class of reactants explained (ref. 1) the paradoxical results that we had found: a reactivity reversal and a sequential reactivity when benzyl chloride and benzyl alcohol compete for Friedel-Crafts alkylation of an aromatic hydrocarbon, such as toluene (ref. 2), on the surface of the "clayzic" catalyst (refs. 3,4) consisting of zinc chloride impregnated on the K10 montmorillonite clay.

CHARGED ALUMINOSILICATE SHEETS

Since the actual examples chosen for this study, because of their prowess as heterogeneous catalysts are modified clays (refs. 5,6), a short summary of the main structural features of such solids is in order. Clays are crystalline aluminosilicate minerals. With a lamellar organization, they consist of layers formed by octahedral AlO_6 aluminate modules and tetrahedral SiO_4 silicate modules as the building blocks. For instance, kaolins (china clay) are 1:1 clays consisting of one octahedral layer bonded to one tetrahedral layer through bridging oxygens. Montmorillonites are 2:1 clays in which one octahedral layer is sandwiched in-between two tetrahedral layers.

Nature ill-behaves with respect to this ideal picture. Sometimes, in a montmorillonite clay, one finds an Al(III) cation replacing a silicon (IV) in the tetrahedral layer. Such a substitution, since the electronic charge from the adjacent oxygens is no longer balanced, leads to an excess of negative electric charge. Because proton transfer is fast, this negative charge spreads itself on the surface oxygens of the whole exposed silicate sheets. And it has to be compensated by counterions, if overall electroneutrality is to be maintained. Furthermore, isomorphous substitution is not restricted to the tetrahedral layer. The octahedral layer is also affected, divalent ions such as Cu(II), Fe(II), Mg(II) or Mn(II) substituting for the Al(III).

Clays for this reason are ion exchangers. A typical montmorillonite has an exchange ability of the order of 100 millimoles of univalent M^+ cations per 100 g of clay. The samples we have focussed on more particularly in this study are made of saponite, the soap stone. A member (like montmorillonite) of the smectite i.e. of the swelling family of clays, saponite is also a 2:1 clay associating one octahedral magnesia layer sandwiched in-between two silica layers. It is a trioctahedral clay, three octahedral sites out of three are occupied by Mg(II) ions, by contrast with dioctahedral clays such as montmorillonite in which two out of three octahedral sites are occupied, usually by Al(III) as we saw. The ideal metallic composition is thus $Mg_6(Al_1Si_7)$. A net negative electrical charge on the layers stems from Al-for-Si substitution in the tetrahedral sites, partially compensated by substitution of trivalent ions into the octahedral sites. Natural saponites have a charge density typical for a smectite, in the range 0.8 to 1.2 per $O_{20}(OH)_4$. The interlayer cations, needed for preservation of electroneutrality, are in the range 60 to 100 meq/100g (ref. 7).

RESIDUAL QUADRUPOLEAR SPLITTINGS

A large number of nuclei combine possession of a magnetic moment and of an electric quadrupole moment. While the former makes them nmr-receptive, the latter (expressing a non-spherical distribution of electrical charge in the nucleus) interacts with local electrostatic field gradients. The energy of interaction, in the kHz to MHz range, is termed the quadrupolar coupling constant (ref. 8). Degeneracy of allowed nmr transitions for a quadrupolar nucleus is lifted by such coupling to a non-vanishing electrostatic field gradient. In the presence of local order, these no longer degenerate transitions give rise to 2I separate absorptions, where I is the nuclear spin quantum number. The pioneering work by Woessner showed as early as 1969 that deuterium residual quadrupolar splittings for D_2O solvent molecules in the presence of suspended clay particles are due to preferential orientation of water molecules affixed to the clay platelets (ref. 9), themselves oriented by application of the very strong B_0 directing field within the magnet of the nmr spectrometer (refs. 10,11). The observed residual quadrupolar splitting has a value dependent upon the orientations of the molecular axes of the water molecule (molecular referential) relative to the clay interface (director referential), and of the clay platelet relative to the applied magnetic field (laboratory referential). A useful theory of the phenomenon, which of course is not restricted to water but observable in principle with any solvent molecule having quadrupolar nuclei, was provided by Swedish workers in 1981 (ref. 12).

In aqueous suspensions of a clay, only a minute fraction of the water molecules (one in ten thousands is the order-of-magnitude) is in contact with the solid particles. Furthermore, these interfacial water molecules exchange fast with bulk water molecules, at ambient temperatures. Only a time-averaged resonance is measured. Accordingly, the residual quadrupolar splitting is also a tiny fraction of the quadrupolar coupling constant. The leverage comes from the large values of the quadrupolar coupling constant. If one considers the deuterons in heavy water, with their quadrupolar coupling constant of 210 kHz, if only one D_2O molecule in 10^4 is ordered at the clay surface, the expected residual quadrupolar splitting is 21 Hz, as the weighted average between the free (0 Hz) and the bound (210,000 Hz) sites. Such a value is indeed representative of the actual, observed cases. Thus, one is provided with a powerful magnifier to focus exclusively on those solvent molecules at the interface of the suspended solid particles.

SOME RESULTS

Let us give an illustration, displacement by quaternary ammonium ions of lithium counterions at the interface of clay platelets. The sample consists of the homoionic lithiated saponite clay suspended in heavy water (20 g.L^{-1}):

TABLE 1. Decrease of the residual quadrupolar splittings for various species as a function of increasing amounts of tetramethylammonium ions.

conc, mM	0	1.82	3.65	7.30	10.92	14.60	18.24	29.20
Li-7, Hz	198	176	150	89	58	53	40	45
O-17, Hz	260	213	194	149	104	95	71	67
H-2, Hz	37	38	31	30	26	25	16	15

The interpretation is that $+NMe_4$ ions displace Li^+ ions from the charged interface till a monomolecular layer of ammonium ions is established (ref. 13). This shows up not only from the lithium ions standpoint but also from that of their hydration molecules.

THE WATER-ACETONITRILE SYSTEM

This binary solvent mixture is of interest for its plausible prebiotic relevance, its role in atmospheric chemistry and its frequent use in mechanistic organic chemistry. Many fine studies have been devoted to this important system, whose structure is rather well understood at the different compositions. Acetonitrile-water mixtures exist as three distinct types. At high acetonitrile content, above a mole fraction of 0.75, water molecules disrupt the structure of liquid acetonitrile. The medium range (mole fraction of acetonitrile 0.2 to 0.75) is one of microheterogeneity with disruption of both acetonitrile and water structures, even leading to demixion at 38 mol% acetonitrile (272K). At low acetonitrile content (mole fraction below 0.2), acetonitrile molecules respect the water structure, perhaps even enhance it slightly, sneaking into the cavities that coexist with the hydrogen-bonded microdomains. The new vista from recent molecular dynamics simulations is that addition of acetonitrile to water enhances the radial correlation of water molecules, while (also at low acetonitrile content) the acetonitrile dipoles arrange themselves antiparallel to one another (ref. 14).

SAPONITE SUSPENDED IN ACETONITRILE-WATER

We adopted as our reporters of the ordering occurring in the interfacial region the ^2H and ^{17}O nuclei for (heavy) water; ^2H and ^{14}N for acetonitrile- d_3 ; and of course ^7Li for the lithium counterions. The information that these nuclei provide – to be presented and discussed in detail elsewhere (ref. 15) – is precise and reliable. An internal check is provided by the handsome intramolecular correlations within the water and the acetonitrile molecules: indeed both nuclei see the same molecular acquisition of order.

As the acetonitrile content of the binary solvent mixtures is raised, more and more lithium ions are extracted from the Stern into the Gouy-Chapman diffuse layer. This is seen from the gradual decrease in the observed residual quadrupolar splitting for the lithium ions. Another, more surprising conclusion, is that of compartmentalization. The water and the acetonitrile molecules display totally decorrelated residual quadrupolar splittings. A possible explanation is that stacks of saponite flakes segregate layers of CD_3CN and D_2O molecules apart from one another. At low acetonitrile content (<20%), some CD_3CN molecules order themselves together with the lithium ions at the clay interface, as seen from strongly correlated residual quadrupolar splittings. They follow the migration of the lithium ions away from the interfacial region. At 20 vol% CD_3CN , these acetonitrile molecules orient themselves, on the average, at the magic angle with respect to the clay surface – the $(3 \cos^2\theta - 1)$ term in the numerical expression of the quadrupolar splitting goes to zero, and so does the ^{14}N residual quadrupolar splitting, which henceforth proceeds to change sign –. Up to a composition of 50 vol% acetonitrile, the average orientation of the interfacial acetonitrile molecules appears to change continuously with composition of the binary solvent mixture. In the whole 0-50 vol% acetonitrile concentration range, conversely, water orientation at the clay surface remains invariant.

CONCLUSIONS

Some of the findings from these studies are disturbingly anti-intuitive. One such finding was differential line broadening. It is rare to find, in nuclear magnetic resonance, unequal widths for the two components of a doublet. This observation, after the attendant experimentation and theorization, was pinned on the cross-correlation of two relaxation mechanisms, dipolar and quadrupolar: the paramagnetic impurities in the clay, iron especially, offer a relaxation pathway competitive with quadrupolar relaxation (ref. 16).

Now to a strange fact about competitive solvation: since water coordinates lithium cations more strongly than acetonitrile molecules do, we had not foreseen that, at least at the boundaries with the suspended saponite flakes, the acetonitrile molecules would follow the lithium ions, leaving behind the water molecules gripping tightly the solid interface.

There is thus ample justification, from such discoveries, in pursuing these types of studies. They are complementary furthermore of earlier work in which other, more readily accessible nmr observables for quadrupolar nuclei (chemical shifts and relaxation rates) were drawn upon for a picture of preferential solvation in the bulk of binary solvent mixtures (refs. 17,18,19).

Then, why wait so long to take advantage of the information available from residual quadrupolar splittings about solvent effects at boundaries? The answer is because some of the necessary technology was unavailable. A case at hand is that of quadrupolar nuclei giving rise to resonances so broad as to demand a deconvolution procedure to extract the desired quantity, which may be unreliable. Oxygen-17 is such a nucleus. Accordingly, double quantum procedures were designed to solve such problems and have become available only recently (ref. 20).

To find out the details of structuring at boundaries, as opposed to bulk properties, has great importance towards elucidation of the factors responsible for reactivity at surfaces, be they those of enzymes or of inorganic solids, of which chemical industry makes such important use with heterogeneous catalysis.

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