7122 *J. Phys. Chem. A* **2006,** *110,* 7122−7129

The Liquid Water−Benzene System

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Received: September 30, 2005; In Final Form: April 4, 2006

The 500 MHz NMR spectra of water−benzene solution near saturation at 303.15, 323.15, and 343.15 K indicate that there is a proton−proton exchange between the water and benzene molecules. In the solution water appears to be present as a dimer attached to the benzene π cloud on one side of each of the two (initially degenerate) fundamental energy levels, as predicted by the Jahn−Teller effect. This view is reinforced by the fact that one of its hydrogen atoms hovers above one of the carbon atoms and the other three are spread upward around the C6 axis of the benzene molecule. It is also supported by the calculated NMR spectra. Both effects are responsible for the change in the NMR spectra of the water molecules from a single line into four AB signals.

Introduction

The behavior of water in a hydrophobic medium is a very important phenomenon that attracts much attention due to the immense possibilities of different interactions, especially in systems of biological interest. This is due to the fact that water is almost never totally insoluble in a hydrophobic medium, especially in the liquid state. The solubility may be as low as a few parts per million, but it cannot be disregarded. On the other hand it is well-known that water is very capable of interacting, forming bonds in many ways both through the hydrogen atoms and the oxygen nonpaired electrons. Therefore the question that immediately arises regards the nature of the interaction, in a solution, between the water molecules and those of the solvent.

One very interesting case is that of the water in benzene system, because of the substantial nonbonded electron clouds in both molecules and especially because of the possibility of an interaction between the hydrogen atoms and the benzene π cloud. The behavior of this system has been extensively examined by many authors, both theoretically and experimentally. Some of the latter in the vapor phase and others as liquids (see refs 1−6 and references cited therein).

Although the solubility of water in benzene is quite low, 707 ppm at 298.15 K,[5] the existence of a solute−solvent interaction product has been generally accepted, especially as the result of dielectric studies. This is so because the very substantial difference in permittivity (ϵ) of both components ($\epsilon = 2.2727$ for benzene and $\epsilon = 78.5$ for water (both at 298.15 K)) makes the procedure especially appropriate for this purpose.

The important advantage of dielectric measurements is that they are very sensitive to changes in the nature of the interaction products. This is an especially valuable indicator at very low concentrations when, regardless of the polarity of the components, the permittivity, though not the result of the simple addition of the values of the pure components, is a linear function of concentration. So much so that if there is an interaction product and its nature changes with concentration, the slope of the line representing ϵ vs concentration should change abruptly without affecting the linearity of each section. This is precisely the case of the alcohols in benzene in the 293.15−333.15 K range of temperatures.[7] The absence of an inflection point in the ϵ vs concentration graph of the water−benzene system definitely confirms that there is only one type of interaction product present,[5] but its nature is by no means clear. The ratio of the components does not depend on the concentration of the solution, indicating that the interaction product remains unchanged over the whole range of concentrations. Furthermore there does not seem to be any influence of the method of dissolution, as shown by the fact that the graph of permittivity vs concentration is independent of the method used to dissolve the water. Either through direct dissolution or isopiestic equilibration as defined by Glasstone[8] and described in detail by Christian et al.,[9] Dailey et al.,[10] and Brubacker et al.[11] This latter procedure provides a saturated solution of water in benzene through vapor pressure equilibration in a closed temperature controlled vessel.

Consequently, for a long time there existed doubts regarding the exact nature of the solute−solvent interaction product, especially as to whether water was present as a monomer or as a cluster of two or more molecules.[6] Although recent work tended to support the existence of a 1:1 interaction product (even called heterodimer),[4] further evidence points toward a 2:1 interaction product (called sometimes a heterotrimer).

But this leads to a very interesting situation, because it raises the question of how the water molecules pass from the bulk liquid into the solution, either directly or through the vapor, in exactly the same way, namely, as monomers, dimers, and trimers, etc. The existence of all these, called *water clusters*, has been extensively examined through a number of careful experimental works and detailed calculations, in the bulk liquid,[12] the vapor[13] and the liquid−vapor interphase.[14] The interesting aspect of the last two papers is that they both confirm the fact that water goes from the bulk to the interphase and the vapor, bound in the same manner. In particular Pfeilsticker et al.[13] consider that water is present in atmospheric air, at 298.15

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10.1021/jp0555908 CCC: $33.50

K, as a dimer with a very small proportion of monomer (1:1000). They further consider the existence of higher clusters [$(H_2O)_n$ with $n \leq 6$] very unlikely, but not impossible.

At this point it seems necessary to discuss briefly a nomenclature item because what results from the interaction of water and benzene molecules is called, as mentioned above, by different names: complexes, clusters, and heteromers. According to the IUPAC'S *Gold Book*,[34] a *complex* is defined as a molecular entity formed by loose association involving two or more component molecular entities (ionic or uncharged), or the corresponding chemical species. The bonding between the components is normally weaker than in a covalent bond. The term has been used with a variety of shades of meaning in different contexts; it is therefore best avoided when a more explicit alternative is applicable. As for the terms *cluster and heteromer*, there are no definitions in the *Gold Book*, so that their use is open to the discretion and or opinion of whoever needs them.

Therefore, since the result of the interaction between water and benzene molecules does not seem to fall within any of the accepted definitions, we prefer to use the expression *interaction product* as a suitable name for what we are seeing.

Cheng et al.[4] and Nakahara et al.[15] reached similar conclusions. However better results for this problem were obtained by Kusanagi[16] studying the NMR spectra of O^{17} in a 20% O^{17}-enriched water as a function of the water content. They reported two signals, a low-field singlet and a higher field triplet. The singlet was assigned to clusters of bulk water, because its size was concentration-dependent. The 1:2:1 triplet, with a measured J coupling of 79 Hz, was identified as due to the J coupling of two hydrogen atoms. The accepted value in this case is 80 Hz.[16]

The single line of the bulk water does not show any fine structure due to the fast exchange typical of hydrogen atoms. The absence of fast exchange in the triplet was considered to be evidence for the existence of only one water molecule. The singlet corresponds to the signal of liquid water that appears around 4.5 ppm and can be observed in any NMR spectrum. On the other hand the triplet, although interesting, does not give meaningful information as to the nature of the interaction product.

These results strongly support what had been observed through dielectric studies in the sense that in solution there is only one kind of interaction product, over the whole range of concentrations. However, the reported data, although tending to support the existence of a 1:1 interaction product, appear to be insufficient to be conclusive. The next step then is to attempt to find an answer to this question.

Infrared studies in the gas phase on the water−benzene "cluster" by Pribble and Zwier[17] show absorptions at 3722, 3706, and 3608 cm^{-1}. These authors assigned the latter to one of the O−H bonds oriented toward the π cloud and the former two as donor and acceptor free O−H transitions. These values are in substantial agreement with those found in solution by Greinacker et al.[18] and in a previous work by one of us,[5] at 3675−3678 cm^{-1} and 3591−3595 cm^{-1}, respectively. Although these results tend to suggest the existence of, at least, a major proportion of the so-called heterotrimer [benzene−$(H_2O)_2$], the simultaneous presence of other clusters cannot be discarded from the IR evidence.

A very interesting and detailed discussion of the IR spectra of the water−benzene system was made by Dobrowolski and Jamróz.[19] They found essentially similar absorptions but made a more detailed and careful analysis of them. They suggested that there is one hydrogen atom of the water molecule that is bound to the benzene π cloud, breaking the C_{2v} symmetry of the water molecule. However they do not make any suggestion whether this bound water molecule is single or part of a "multimer", leaving open the question of the nature of the water−benzene interaction product.

Also some very interesting results are those reported by Susuki et al.[1] and Augspurger et al.[2] in the gaseous phase, because they claim a 1:1 interaction product and suggest a hydrogen-bond-like link, between only one of the water hydrogen atoms and the system of the π electrons of benzene. However the situation in solution still remains unanswered and very especially in the liquid phase at room temperature and atmospheric pressure.

The experimental results available at present from dielectric studies and IR and NMR spectroscopies, although very interesting, are by no means conclusive. They do confirm the existence of a water−benzene interaction product but are insufficient to indicate its nature; therefore a different experimental approach seems to be necessary to overcome this difficulty.

On the other hand a substantial amount of theoretical work has been reported in recent years on the structure, stability, and characterization of the possible benzene−water complexes[17−23] and the strength and identification of the benzene−water hydrogen bond.[24, 25]

In this respect the theoretical studies on the benzene−$(H_2O)_n$ "complexes" by Augspurger et al.,[20] Grunwald and Steel,[21] and Fredericks et al.[22] also tend to favor a 1:1 interaction product (in other words a so-called dimer) with one water proton pointing toward the benzene π cloud and the other one away from it. Theoretical studies by Feller[23] and Novoa and Mota[24] appear to confirm the existence of a hydrogen-bonded 1:1 interaction product, or dimer as they call it. It is interesting to note that in both cases the authors propose a molecular distribution whereby one of the water protons is located "hovering" above the center of the benzene π cloud while the other one tends to point toward one of the ring protons.

However all these results lead to a different view of the system as compared to that mentioned in the work on water in atmospheric air,[13] wherein the presence of a dimer (water dimer) with a very small proportion of monomer is claimed to exist in air. This would lead to an interaction product resulting from the simultaneous presence of both a water dimer and a small amount of water monomer.

Therefore it can be said that since the mentioned recent studies refer to the gaseous phase and that those in solution are not conclusive, the essential question remains unanswered. It is actually 2-fold: (1) What is the composition of the interaction product in the liquid phase at room temperature and atmospheric pressure? (2) What is the location of the water molecule (or molecules) in it?

The subsequent step is then to verify what happens in the liquid state and above all in the range of room temperatures, because it is under these conditions that many interactions become important in systems containing water and a hydrophobic medium like benzene. A very important limitation must be kept in mind at this point, namely, the boiling point of benzene (353.15 K) because it prevents examining the liquid system at higher temperatures.

In this work we attempt to answer the above-mentioned 2-fold question through 500 MHz NMR spectra of ^1H in benzene and deuterated benzene, respectively, close to saturation with water and with D_2O. It was hoped that the use of deuterated compounds would lead to simpler spectra, easier to analyze and interpret. This approach was chosen because it was expected that at 500 MHz the spectra would provide evidence to point toward an adequate solution.

Experimental Section

The compounds used were as follows: deuterated benzene (99.96%, Sigma Chem. Co.), D_2O (99.9%, Sigma), and conductivity water kept in a quartz Erlenmeyer flask and carefully purified benzene. The latter was obtained by fractionally crystallizing twice reagent grade benzene that was then refluxed over sodium ribbon, under dry nitrogen, until dryness through the blue reaction with benzophenone.

The solutions were prepared by direct dissolution under nitrogen to avoid any contamination of atmospheric moisture and kept below saturation at 298.15 K; their components were the following: benzene/water, benzene-d_6/water, and benzene/D_2O.

Direct dissolution was preferred not only to minimize the risk of contamination with atmospheric moisture but also to be sure that the concentration at room temperature (∼298.15 K) remained below saturation. Since the accepted value for a saturated H_2O in benzene solution is 707 ppm at 298.15 K, solutions were prepared by dissolving 0.006 g of water or D_2O in 9.47−9.52 g of benzene or benzene-d_6, which means concentrations of 630−640 ppm. All samples were kept under dry nitrogen with a tight stopper. It is important to keep the concentration at 600 ppm, to be far enough below saturation so as to avoid the formation of visible water droplets. These would immediately show the pure water signal at about 4.5 ppm, as indicted above. Consequently in the NMR spectra at 303.15, 323.15, and 343.15 K there is no risk of water coming out of solution with the subsequent formation of water microdroplets, because the temperature is kept 10 K below the boiling point of benzene. This was confirmed through the absence of the bulk water signal in all the NMR spectra. Also, keeping the sample temperature 10 K below the boiling point of benzene prevents any substantial change in concentration due to solvent evaporation.

The 500 MHz spectra were obtained on a BRUKER AM 500 instrument at 303.15, 323.15, and 343.15 K, as given by the spectrometer sample temperature control. A deuterium signal was used to lock the field in the usual manner, and the residual proton signal (due to C_6D_5H) was used as a reference, assigning to it a value of 7.15 ppm on the tetramethylsilane (TMS) scale (Figures 1−3).

Each of these spectra was obtained using only eight scans, with the normal cyclic routine, using 32 K of memory to get at least five points per hertz. To improve the resolution, it was necessary to use some resolution enhancement by a mild "Gaussian multiplication". Nevertheless, the line width obtained was always not less than about 2 Hz, this rather big line width being due to the fast exchange.

H/D Exchange. In the freshly prepared benzene-d_6/H_2O the signals discussed below appear clearly but start weakening after a few hours and disappear completely in 24 h. On the other hand in the freshly prepared benzene/D_2O solution the high-field region is at first empty of signals, but those observed in the former solution start appearing after a few hours and are quite strong after 24 h. Therefore care was taken to obtain the spectra on the freshly prepared solutions.

NMR Spectra. Two groups of lines can be seen (Figures 1−3), one at 0.85 ppm and the other at 1.35 ppm. Referring now the positions of these groups to the bulk water signal (4.5 ppm), the difference gives us what is called the shielding factor, which, in our case, is 3.65 and 3.15 ppm, respectively. Now if we assume that these NMR signals are due to water molecules and we look at the isoshielding graph of Bovey et al.,[27] then we must conclude that all these water molecules are above and very near the π electron cloud of benzene. Also their locations must differ so that the field of the ring will create a difference in shielding.

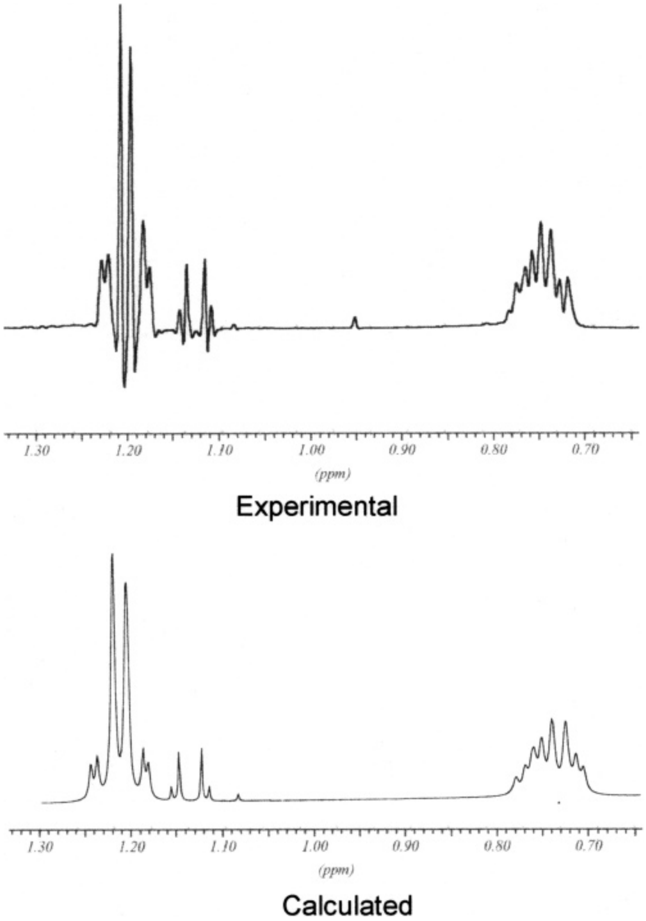

Figure 1. NMR spectrum at 500 MHz at 303 K: (a, top) experimental; (b, bottom) calculated.

Four AB signals in total are seen. For the calculated spectra the analysis is as follows.

The parameters of each AB set (that is just a textbook case) can be obtained directly from the line frequencies: if we call a the distance between the small AB lines and b that between the big ones, then the coupling constant $J = (a - b)/2$ and the chemical shifts difference between the two protons is $\sigma = \mathrm{SQR}(ab)$. At this point it is noteworthy to point out that the ratio of the intensities between the big and the small lines is simply a/b.

The following are the parameters of the main AB groups, as deduced from the experimental line frequencies, using first the spectrum of the left side group obtained at 323.15 K (Figure 2), which was found to show the best resolved AB spectra,

$$\sigma_1 = 12.2\ \mathrm{Hz} \quad \text{and} \quad J_1 = 10.6\ \mathrm{Hz}; \qquad \sigma_2 = 10.3\ \mathrm{Hz} \quad \text{and} \quad J_2 = 6.8\ \mathrm{Hz}$$

and, in the right side, the high-field group,

$$\sigma_1 = 11.6\ \mathrm{Hz} \quad \text{and} \quad J_1 = 9.1\ \mathrm{Hz}; \qquad \sigma_2 = 9.6\ \mathrm{Hz} \quad \text{and} \quad J_2 = 5.3\ \mathrm{Hz}$$

It may be interesting to compare these results with the known value of the indirect spin−spin coupling constant J between

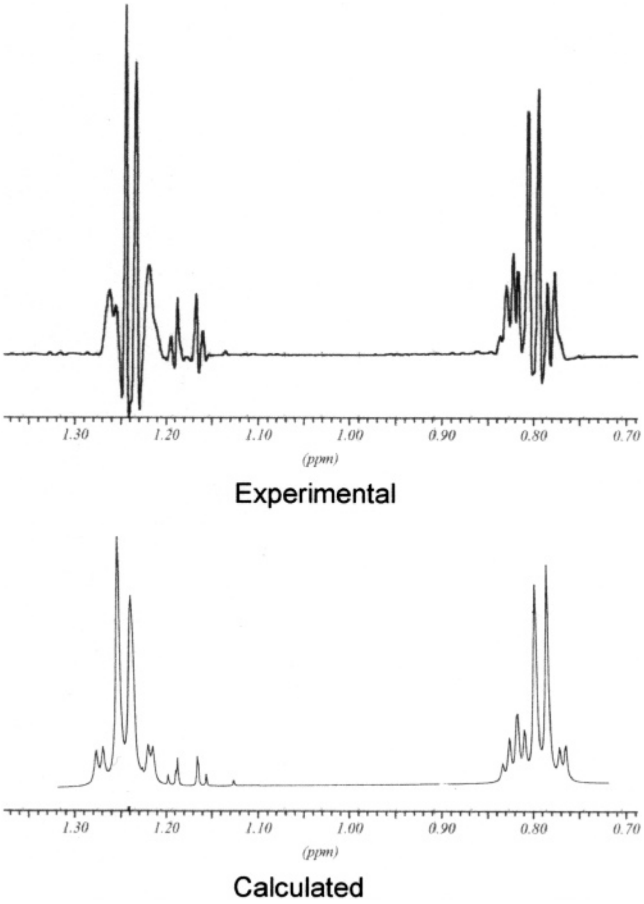

Figure 2. NMR spectrum at 500 MHz at 323 K: (a, top) experimental; (b, bottom) calculated.

the two water hydrogen atoms. This can be deduced from the absolute value of the measured constant $J_{H,D} = 1.12$, multiplying this value by 6.55. The gyromagnetic ratio of these nuclei then gives $J_{H,H} = -7.336$ Hz. And for each AB case of our problem, one J constant is bigger and the other smaller than the “normal” J value, the average of all of them being 7.95 Hz.

Finally it is important to mention here that both groups of signals have exactly the same areas, which is a clear indication of the absence of any other interaction except that of water and benzene.

Results and Discussion

Two aspects have to be distinguished clearly, the proton exchange and the identification of the interaction product. So they will be considered separately.

Proton Exchange. As anticipated in the Experimental Section, there appears evidence of exchange of protons between water (either H_2O or D_2O) and the benzene (either protonated or deuterated) molecules. The evidence for this result is that in the benzene/D_2O and the benzene-d_6/H_2O, the spectra show a marked difference when taken immediately after the solution has been prepared and hours later.

Therefore it can be concluded that there is a H/D exchange between the water and benzene molecules. This is not altogether unexpected since there are recent reports by Bakker and Nienhuys[25] that indicate H/D exchange in water and by Ibrahim et al.[26] that found deprotonation in the benzene$^+$−water system.

Water−Benzene Interaction Product. Since the possible existence of an interaction product was studied through NMR spectra, this part of our discussion will refer directly to them.

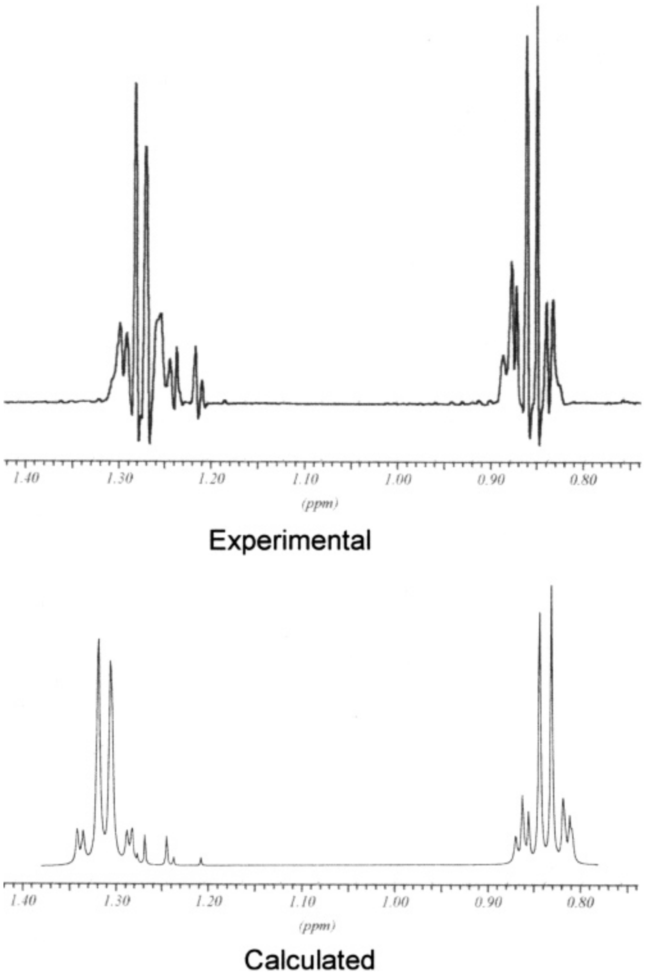

Figure 3. NMR spectrum at 500 MHz at 343.15 K: (a, top) experimental; (b, bottom) calculated.

To begin with, the NMR spectrum of pure water shows only one signal at about 4.5 ppm in the customary scale, because the two hydrogen atoms in the molecule are surrounded by identical electronic atmospheres. The position of the groups we observed in the spectra to the right of the normal water signal is the result of the “deshielding effect” of the benzene ring. However if, for some reason, the two hydrogen nuclei would be surrounded by different electronic atmospheres, each one of the hydrogen atoms would show its own signal. In this case the NMR spectrum would become one of the AB type with a group of four lines, one pair not far from another and of different intensities. The two closest lines would be the more intense ones and the other two would be the weaker ones. The characteristics of these spectra can be easily calculated from the parameters provided by the pertinent theory.

As indicated the NMR spectra show two groups of lines, one at about 0.85 ppm and the other at about 1.35 ppm, on the standard NMR scale in which the signal of imperfectly deuterated benzene is assumed to be at 7.15 ppm. As already indicated, the areas of these two groups are identical, as shown by the NMR instrument software.

Each of these groups is formed by three NMR spectra of the AB type, two of them superposed because they have the same position on the NMR scale and the same relative intensity, as verified by computer simulation. The third AB spectrum, of much lower intensity, will be considered later in this discussion.

This could be interpreted as the spectrum of four water molecules, two in each group, probably bound to the π electron cloud of benzene. Then, as a result of the change in electronic atmosphere of the water hydrogen atoms, now bound to benzene, each would show an AB type spectrum of four lines instead of the expected single line. But this cannot lead one to assume that there are four water molecules bound to some benzene, because at this point the so-called "NMR time scale" must be considered, meaning that what is observed is the superposition of the spectra of different molecules of similar structure.

Both of the above indicated groups have the same structure: two big lines and four small ones. This, a rather unusual NMR spectrum, can be interpreted as due to two superposed AB spectra, each one with its own *J* coupling constant but both with the same, or almost the same, chemical shift. Each AB spectrum can be considered to be due to a difference in the effects of the benzene electron cloud on the two hydrogen atoms of the water molecule, when it is linked to benzene. As a consequence the single-line NMR spectrum of water (a typical A_2 spectrum) becomes the observed typical AB spectrum.

The question now is as follows: Why are there two AB spectra in each group? This could be due to the existence of two different places where water molecules can attach to benzene, each molecule by "its own" hydrogen bond. For this the Jahn−Teller effect should be considered, since it implies the breaking of the degeneracy of the fundamental electronic level of benzene into two parts, each with a slightly different energy value.[28] The two different AB spectra can now be interpreted as the result of the difference in electron atmosphere acting on each water proton leading to different chemical shifts and the consequent location of the AB type signals. Furthermore the water protons have two possibilities to form a hydrogen bond: either with one level or with the other. Since the energies of these levels are different, it is reasonable to consider that their effect on the water hydrogen atoms will also be different.

Again this looks as if in each group of signals there were two water molecules at the same time, a total of four water molecules for each benzene molecule. Or that only two water molecules are attached to a benzene molecule, one in each group.

However this raises the following question: How many water molecules are actually attached to each benzene molecule at any time? To answer this, it is necessary to take into account what is called "the NMR time scale": that whenever the NMR sample is a mixture of molecules, e.g. of the same kind but with different substituents, the NMR spectrum becomes the superposition of the spectra of the different molecules, as if all were there at the same time. The next step it to examine the several possibilities for this to happen.

We shall first assume that in the solution water is a monomer (that is, just H_2O). Then, as judged from the NMR spectrum, there are four different places where it can become "attached" to the ring. This must be always to the fundamental state of benzene. But, this state is doubly degenerate and, according to the Jahn−Teller effect, it is unstable and splits into two parts, breaking the degeneracy. This is considered the reason for the existence of the two, quite similar AB spectra in the same place, of the same intensity though of a different *J* coupling constant (since there is no reason to consider these two possibilities to be of different probability). Therefore there are benzene molecules with water attached to one or the other of the fundamental possible states, but only one at any time.

However, since there are two groups, it can be assumed that there are two different places where water can become attached to, either to one or the other of the Jahn−Teller states, leading to the left or to the right group of signals. Both are equally probable as shown by the identity of the areas of the two groups.

Therefore, it can be assumed that a water molecule has four possible ways to become attached to benzene. But there is no reason to consider that the probability of becoming attached, leading to either the left or the right group, should be the same. On the contrary, the "deshielding effect" of the π electron system shows that the two groups are at a different distance from the axis of the system and, therefore, at a different place of the π electron system.

At this point one alternative is to assume that there are two water molecules attached simultaneously to the same benzene ring. But this is highly improbable because, at the concentration used in our samples, there are about 1600 benzene molecules for every water molecule in the solution. Therefore, the probability of a benzene molecule to get one water molecule is less than 10^{-3} and that of attaching two of them is, according to the laws of probability, less than 10^{-6}, and 10^{-9} for three, and so on. According to the probability laws, the simultaneous meeting of two independent water molecules with the same benzene molecule is highly unlikely.

Now, since the position of the two groups is so clear, it seems more likely to consider that what reaches a benzene molecule are two water molecules, but that they are bound together in a somewhat rather rigid way (a dimer). For the reasons discussed above we prefer to use the word dimer to designate the product of the union of two molecules of the same species. This would leave the terms heterodimer and heterotrimer, etc., used by some authors[4] for products of the union of molecules of different species, although we still prefer to talk of an interaction product in the present case.

Therefore it can be concluded that what is being seen in the NMR spectra is the result of two water molecules (as a pair or a dimer) that arrived at the same time, to a certain benzene molecule. In the dimer the water molecules are bound (asymmetrically) by "their own" hydrogen bond and have a more or less fixed (asymmetric) position among them. This leads to the two groups of lines, one group for each molecule of the water dimer, with the two AB NMR spectra in each group, that are seen simultaneously. They are different depending to which of the two fundamental levels the hydrogen atoms are then attached to. Considering now that the shielding is different in both levels of benzene, any difference in the peaks can be justified.

This reasoning points toward the existence of water as a dimer in the solution with benzene. Then, since there are two fundamental, now nondegenerate electronic levels in the benzene molecule,[28] any water dimer gets bound to either of the two levels, of which there are only two possibilities: either one water "high" and the other "low" or one "low" and the other "high".

At this point it must be remembered that what we apparently see as a single spectrum is, in fact, a superposition of the spectra of different benzene molecules, each one with its "own" water dimer, attached to a different (now not degenerate) level. All this is due, as already mentioned, to what is called the NMR time scale.

This, as well as the previous considerations, leads us to accept that water arrives at the benzene molecule already as a dimer and that there are therefore always two, and only two, water molecules attached to a benzene molecule. This assumption is also favored by what was described in the experimental part, that both groups have exactly the same area.

Now the small AB type spectra, mentioned above as the third AB spectrum of much smaller intensity, can be evaluated. They can be attributed to some dimers becoming attached to other, nondegenerate, also low-energy levels, of benzene. NMR measurements indicate that this occurs at about 11% of the total.

In this respect it was already stated that the total integrals of both groups are of exactly the same area. An integration of the left small AB group, which is well separated from the big lines, showed it to be 11 % of the total. In view of the exact equality of the total areas, the small right-hand group (the integral of which could not be made because of its partial overlapping with the big lines) must also be 11 % of the total. Evidently these percentages coincide with those of the two energy levels and, consequently, support the assumption that the pair of small AB signals must also be due to a dimer.

The effect of the temperature on these "small" AB spectra is perhaps noteworthy, as can be seen in the figures. With increasing temperature, the four weak lines in the low-field group shift to the left, while the four small AB lines of the high-field group shift to the right. In both cases they "try to join" the big ones.

Together with the above discussion the multiplicity of signals questions seriously the possibility of having only one water molecule bound to one benzene molecule. In other words it does not support the existence of a 1:1 interaction product and favors, at least, a 2:1 interaction product. This is in line with the evidence found regarding the transfer of water through air from bulk to solution[13] and could also suggest some explanation of the additional weaker lines.

The presence of the "sets of four lines" suggested the possibility of a computer simulation of the NMR spectra as a mixture of AB cases, and what we see in our NMR spectra is just the sum of all the signals of the molecules of benzene that have water molecules somewhere attached to them. The good coincidence observed between the experimental and calculated spectra allow one to rule out other possible interpretations such as the existence of higher spin systems, benzene−benzene interactions, and the interaction of two benzene molecules with one water molecule.

Since a priori we know nothing about the relative populations of the different AB sets, these must be estimated, considering that in the strong pairs the intensities of both components seem to be alike. A program was written and the parameters adjusted by trial and error. The results of this simulation can be seen in the accompanying Figures 1b, 2b, and 3b. Where there is a substantial resemblance between both groups of lines.

To sum up it can be said that the hypothesis to monomeric water entering into solution requires that the benzene molecule show two different possible sites for adherence. This is highly unlikely not only due to the complex structure of the π electrons cloud but also because the statistical probability of two water molecules finding the same benzene molecule is less than 10^{-6}. Furthermore if two such sites would exist, it is also highly unlikely that they should have the same probability of adherence. This would lead to two different areas of the two groups. That is evidently not the case. Conversely the dimer hypothesis explains the existence of two groups of signals of identical areas.

Considering now Bovey's curves as a first approximation of the benzene diamagnetic effect, it can be seen that the effect is higher for the group at 0.85 ppm and lower for that at 1.35 ppm. This indicates that the former group is closer to the region near the edge of the benzene ring, where the "demagnetization" of the field is larger. Furthermore that same group shows, at room temperature a larger line half-width than that corresponding to the other group. This indicates that in the region of maximum demagnetization the relaxation process is more effective than elsewhere.

Figure 4. Side view of the interaction product where the hydrogen atom farthest from the π cloud lies away from it.

The water dimer hypothesis is further supported by the fact that the two weak AB type signals that we are assuming adhered to different energy levels than the fundamental have also the same area. If it were a water monomer, there would be only one signal.

The above results and discussion suggest that the water molecules enter into solution already as dimers, that they attach to any side of the benzene molecule π cloud to give rise to all the signals, in the manner discussed above (considering even the two small AB spectra, in the proportion of 89/11), as deduced from the NMR spectra.

Therefore what we have called the *interaction product* is in fact a benzene−$(H_2O)_2$ trimer that remains unchanged throughout the whole range of concentration, as indicated by the unbroken linearity in the plot of permittivity vs concentration.

One additional question that remains to be answered regards the possible position of each water dimer with regard to any benzene molecule. The results described tend to indicate that two of the hydrogen atoms of one of the water molecules, in the dimer, "hover" above the edge of the benzene ring. The other two rise away with one of them near the vertical perpendicular to the center of the π cloud.

The H−O distance in water can be taken to be about 0.96 Å and the H−O angle as 104.5° [20,22,28,30,] so that the two hydrogen atoms in water are separated by about 1.51 Å. On the other hand the -C−C- distance in the benzene ring can be taken as 1.399 Å.[30] Therefore, of the two hydrogen atoms of the water molecule in the dimer, nearest to the π cloud, only one can be above a carbon atom. This leaves the other three hydrogen atoms in different environments and gives additional support to the observed NMR spectra.

Previous studies[2,20,22,24] have suggested a number of possible images for this interaction product, sometimes called a heterotrimer. In all cases just one of the water hydrogen atoms is considered to be over the π cloud, either over one of the carbon atoms or over the center of the cloud. In both cases this would explain the different environments of each of the four hydrogen atoms and the multiplicity of NMR signals. However the question of the position of the remaining hydrogen atoms has still to be explained.

There are essentially the two possibilities: that shown in Figure 4, where the hydrogen atom that is farthest from the π cloud lies away from it, or that shown in Figures 5 and 6. The latter is favored because both water molecules are in the strong positive region of the shielding factors and are quite similar in magnitude (3.15 and 3.75 ppm). On the other hand in the structure shown in Figure 4 the shielding factor of 1 of the water molecules would be negative.

As anticipated in the Introduction, the behavior of water in a variety of media is a matter of considerable importance that has and is attracting much attention, especially due to its influence in electron-transfer kinetics in many systems.[31,32] Consequently the presence of water as dimers under normal

Figure 5. Side view of the interaction product where the hydrogen atom farthest from the π cloud lies over it.

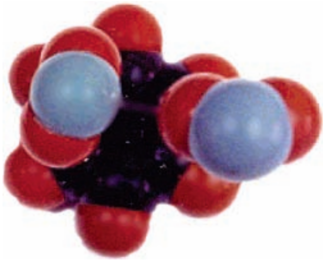

Figure 6. Top view of the interaction product where the hydrogen atom farthest from the π cloud lies over it.

conditions of temperature and pressure ought to facilitate the understanding and interpretation of what is happening.

This appears to be of particular importance in biological systems because they are usually a complex combination of polar, nonpolar, hydrophobic, and hydrophilic components wherein water plays a substantial part in their overall behavior.

Therefore a clear indication of how water may be present is of substantial interest since single molecules or dimers will necessarily behave in very different ways.

Conclusions

Several important consequences emerge from the reported NMR spectra that can be listed as follows;

1. There is a proton−proton exchange between the water and benzene molecules.

2. Water enters into solution with benzene already as a dimer and attaches to the benzene π cloud on one side of each of the two (initially degenerate) fundamental energy levels split by the Jahn−Teller effect. One of its hydrogen atoms hovers above one of the carbon atoms and the other three are spread upward around the C6 axis of benzene.

3. The existence of the two overlapping strong AB systems in each group is due to the Hückel description of the benzene orbitals,[28] the lowest energy orbital being doubly degenerate. Most water dimers attach to one kind of the π orbitals and a few to another one. The first of these perturbations breaks the degeneracy of the benzene, following the Jahn−Teller effect,[28] changing as well the NMR spectra of the water dimer NMR spectrum to an AB case. Since the benzene levels are initially of the same energy, the same should happen with the resultant resonant frequencies of both water dimers, but, being attached to different orbitals, they have different values for the σ and J constants. It is noted that one of these water dimers has a J constant that is larger and the other one that is smaller than the "normal" value of the J constant. Also the different environments of each hydrogen atom are an additional element of proof for the observed complex NMR signals.

4. The multiplicity of possibilities (bond methods) stems from the "electron mobility" in the benzene π cloud. Theoretical calculations, as well as some experimental evidence,[26] indicate that this mobility is by no means regular and perfectly stable, as can be seen in the image obtained by Ohtani et al.[33] with the tunnel effect scanning microscope. The changes observed in the spectra as the temperature increases confirm this suggestion that is also supported by the calculated NMR spectra.

5. The existence of water as a dimer in a hydrophobic medium at normal conditions of temperature and pressure opens new possibilities toward a better understanding of systems wherein electron-transfer kinetics, mediated by the presence of water, is of substantial importance. This is the case in many biological systems.

Acknowledgment. M.B. acknowledges the assistance of the van't Hoff Fond for a grant that made it possible to obtain the needed deuterated compounds. The authors are indebted to Professors Horacio Grimberg (Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Argentina), Gyan Johari (McMaster University, Canada), and William J. Steel (Pennsylvania State University, USA) for valuable discussions and commenting on the manuscript. The authors are especially grateful for the detailed, careful, and enlightening reviews by the reviewers because by pointing out the weaknesses of the original manuscript they helped to make a substantial and detailed revision.

References and Notes

(1) Suzuki, S.; Green, P. G.; Baumgartner, R. E.; Dasgupta, S.; Godard, W., III; Blake, G. A. *Science* **1992**, *257*, 942.
(2) Augspurger, J. D.; Dykstra, C. E.; Zwier, T. S. *J. Phys. Chem.* **1992**, *96*, 7252.
(3) Backx, P.; Goldman, S. *J. Phys. Chem.* **1981**, *85*, 2975.
(4) Cheng, B. M.; Grover, J. R.; Walters, E. A. *Chem. Phys. Lett.* **1995**, *232*, 364.
(5) Barón, M. *An. Asoc. Quim. Argent.* **1979**, *67*, 203.
(6) Christian, S. D.; Taha, A. A.; Gash, B. W. *Q. Rev.* **1970**, *24*, 20.
(7) Barón, M.; Mechetti, H. *J. Phys. Chem.* **1982**, *86*, 3464.
(8) Glasstone, S. *Textbook of Physical Chemistry*, 2nd ed.; Van Nostrand: New York, 1946; p 632 and ss.
(9) Christian, S. D.; Affsprung, H. E.; Johnson, J. R.; Warley, J. D. *J. Chem. Educ.* **1963**, *40* (8), 419.
(10) Dailey, G. W.; Huff, R. B.; Kang, J.; Queen, L. D.; Paterson, C. S. *J. Chem. Educ.* **1961**, *38* (1), 28.
(11) Brubacker, C. H., Jr.; Johnson, C. E.; Knop, S. P.; Betts, F. *J. Chem. Educ.* **1957**, *34* (1), 42.
(12) Liu, K.; Cruzan, J. D.; Saykally, R. J. *Science* **1996**, *271*, 929.
(13) Pfeilsticker, K.; Lotter, A.; Peters, C.; Bösch, H. *Science* **2003**, *300*, 2078.
(14) Marx, D. *Science* **2004**, *303*, 634.
(15) Wakai, M. N. C.; Yosimoto, Y.; Matubashi, Y. *J. Phys. Chem.* **1996**, *100*, 1345, and references cited therein.
(16) Kusanagi, H. *Chemistry Lett.* **1996**, 41.
(17) Pribble, N. R.; Zwier, T. S. *Science* **1994**, *265*, 75.
(18) Greinacker, E.; Luttke, W.; Mecke, R. *Elektochem, Z.* **1955**, *58*, 23.
(19) Dobrowolski, J.; Jamróz, M. H. *J. Mol. Struct.* **1993**, *293*, 147.
(20) Augspurger, J. D.; Dykstra, C. E.; Zwier, T. S. *J. Phys. Chem.* **1993**, *97*, 980.
(21) Grunwald, E.; Steel, C. *Pure Appl. Chem.* **1993**, *65*, 2543.
(22) Fredericks, S. Y.; Jordan, K. D.; Zwier, T. S. *J. Phys. Chem.* **1996**, *100*, 7810.
(23) Feller, D. *J. Phys. Chem. A* **1999**, *103*, 7558.
(24) Novoa, J. J.; Mota, F. *Chem. Phys. Lett.* **2000**, *318*, 345.
(25) Bakker, H. J.; Nienhuys, H. K. *Science* **2002**, *297*, 587.
(26) Ibrahim, Y.; Alsharaeh, E.; Dias, K.; Meot-Ner (Mautner), M.; Samy El- Shall, M. *J. Am. Chem. Soc.* **2004**, *126*, 12766.
(27) Johnson, C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012. Bovey, F. A.; Jelinski, L.; Mirau, P. A. *Nuclear Magnetic Resonnce Spectroscopy*, 2nd ed.; Academic Press: New York, 1988; and references cited therein.

(28) Jahn, H. S. A.; Teller, E. *Proc. R. Soc. London* **1937**, *161*, 220.

(29) Cartwell, E.; Fowles, G. W. A. *Valence and Molecular Structure*; Butterworth: London, 1963; Figure 40.

(30) Sutton, L. E., Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society Special Publication, Nos. 11 and 18; The Chemical Society: London, 1958, 1965.

(31) Otting, G.; Liepinsh, E.; Wüthrich, K. *Science* **1991**, *254*, 974.

(32) Lin, J.; Balabin, I. S.; Beratan, D. N. *Science* **2005**, *310*, 1311.

(33) Ohtani, H.; Wilson, R. J.; Chiang, S.; Mate, C. M. *Phys. Rev. Lett.* **1988**, *60*, 2398. See also the 1988 IBM report with an interesting picture of the benzene molecule, adsorbed on a palladium surface.

(34) IUPAC Gold Book, 2nd ed.; International Union of Pure and Applied Chemistry: Oxford, U.K., 1997, p 81.