



Phenol forms complexes with tetramethylammonium ions in aqueous solution?

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Abstract

Interactions between phenol and the tetramethylammonium (TETMA) ion were studied experimentally by measuring electrolyte conductivity and its dielectric constant and theoretically using the HF/6-31G(d) and B3LYP/6-31G(d) ab-initio levels of theory. In the latter study, the effect of aqueous environment was included by using the solvent reaction field method. The experiment and the theory give evidence for the existence of complexes between phenol and the TETMA ion in aqueous solution. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Aromatic ring–cation interactions have become appreciated as an important nonbonding force in chemistry and structural biology [1–9]. One can rationalize that the main driving force for this type of interaction is the interaction energy ion–quadrupole. The quadrupole mainly originates from the π electrons of the aromatic ring. The main additional interaction energy terms arise from the induced dipoles and charge transfer term. In the present case, there is an additional possibility for interaction between the phenol hydroxyl group and tetramethylammonium (TETMA) ion. High level ab-initio calculations using the method of supermolecules take into account all the energy terms and thus yield a reliable interaction energy. Density functional methods combined with flexible basis sets take into account a significant part

of the dispersion energy that is not taken into account by the Hartree–Fock method.

In aqueous solution, the situation is more complicated, since during the complexation the favourable ion–aromatic ring interaction energy must be traded for partial desolvation (free) energy of both species. It is worth emphasizing that the desolvation of the tetramethylammonium ion is more costly than desolvation of phenol. With the currently available computer power, it is still impossible to treat all the relevant solvent molecules to electronic detail and to perform solvent averaging in order to calculate the free energy difference for such an association process. One can circumvent this difficulty by applying a simplified atom-to-atom potential which enables free energy calculations using molecular dynamics or a Monte Carlo procedure. The drawback is the lack of accuracy resulting from the application of simplified potentials. Attractive alternatives are the solvent reaction field methods, where a solute is embedded in a cavity, while the solvent is represented by a

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dielectric continuum. For a recent review concerning solvent reaction field methods, see the reference of Tomasi and Persico [10].

It is a challenge to confirm experimentally the existence of phenol–TETMA complexes in aqueous solution. The basic idea that inspired the conductivity measurements in the present investigation was the following: due to its larger dimensions the phenol–TETMA ion complex is anticipated to have a lower mobility than the tetramethylammonium ion itself. This means that upon addition of phenol to a solution containing TETMA ions, the overall specific conductivity of the solution should drop. For example, let us assume that the anion in the initial TETMA solution is chloride. The transport numbers of the TETMA and the chloride ion are then 0.37 and 0.63, respectively (as calculated from equivalent conductivity data in Ref. [11]). Provided that all the TETMA ions formed complexes with phenol, and assuming that the mobility of such complexes is vanishingly small, it would follow that the conductivity of the solution containing both phenol and TETMA ions would be 37% lower than that containing TETMA ions only. If, on the other hand, one assumes that the mobility of the complex equals that of the TETMA ion, then the conductivity should not change. Please note that these are the limiting cases.

Impedance spectroscopy is a technique which enables accurate measurements of the conductivity of a solution as well as its dielectric constant at different frequencies (typically in the range of 1 mHz to 1 MHz). Using impedance spectroscopy, very small conductivity changes can be detected. In the present investigation, the estimated lower limit of the sensitivity with respect to conductivity measurements is $\sim 0.2\%$. The measured variation in conductivity, however, is about one order of magnitude higher, which certainly justifies the use of the method.

To summarize, in this Letter we report measurements of changes in conductivity of an aqueous solution of tetramethylammonium chloride upon addition of a phenol solution. The changes in conductivity are interpreted in terms of the formation of tetramethylammonium ion–phenol complexes. In addition, *ab initio* and density functional theory calculations of a tetramethylammonium ion–phenol complex are reported. Effects of hydration are included by the solvent reaction field method.

The organization of this Letter is as follows. After the description of experimental arrangement in Section 2, *ab-initio* results are presented (Section 3), followed by Section 4 containing the impedance spectroscopy measurements together with the results. Section 5 contains a discussion of the results.

2. Experimental

All conductivity measurements were performed using a standard conductometric three-ring two-Pt-electrode cell (HEK 1213, Metrel). The conductivities were determined from the impedance spectra measured in the range of 20 Hz–1 MHz at 20 points per frequency decade using a Hewlett Packard 4284A Precision LCR meter. Within each set of measurements, the temperature was kept at a constant value of 24°C with fluctuations not exceeding $\pm 0.1^\circ\text{C}$. The pH of the studied solutions was measured using a Radiometer PHM92 Lab pH meter. The dielectric constant of the solutions was measured in terms of capacity-vs.-frequency measurements using the same LCR meter as mentioned above. For this purpose we employed a laboratory-made parallel-electrode cell. The electrode area was 42 mm \times 42 mm and the interelectrode distance was 3 mm.

All chemicals used were p.a. and supplied by the following manufacturers: Fluka ($(\text{CH}_3)_4\text{NCl}$), Kemika (LiCl) and Carlo Erba (phenol). The water used for solution preparation was doubly distilled in the laboratory and had a conductivity of $2 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$.

3. *Ab-initio* and DFT calculations

Ab-initio calculations were performed for phenol, TETMA and the complex. A more detailed theoretical study of this and related complexes will be published elsewhere [12]. Species were subject to full geometry optimization. In the geometry optimization of the complex, more than one starting structure was considered in order to prevent the systems becoming trapped in the local minimum. We report only the lowest minimum found. The minimum was proved to be the real minimum, rather than

a transition state, by scanning the intermolecular degrees of freedom around the stationary points.

Ab-initio calculations were performed using the basis set 6-31G(d). This double-zeta basis set augmented with the polarization functions on the heavy atoms is flexible enough to faithfully describe the interaction energy of the medium strong molecular complexes and is still computationally tractable (Fig. 1). Ab-initio calculations were performed at both the Hartree–Fock and density functional B3LYP level. The latter level includes the calculation of exchange functional by the method proposed by Becke [13] and correlation functional suggested by Lee, Yang and Parr [14] and the calculation includes a significant part of the dispersion energy. In the ab-initio calculation of interaction energy, the counterpoise method of Boys and Bernardi [15] was applied to correct for the basis set superposition error. At the B3LYP/6-31G(d) level, the solvent reaction field was included using the method of Miertuš et al. [16] as implemented in Gaussian-94 [17]. Solvent reaction field calculations give rise to free energies of solvation [10], despite all the drawbacks inherent to such calculations (lack of specific interactions, electrons feel time averaged solvent).

The choice of the solute cavity is a crucial element of the solvent reaction field calculations, since the results of the calculations critically depend on the shape and the size of the cavity. Strictly speaking,

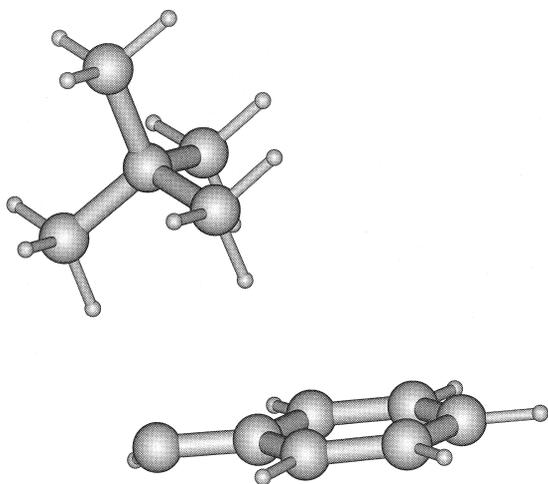


Fig. 1. B3LYP/6-31G(d) fully optimized structure of the phenol–tetramethylammonium ion complex.

such calculations are not ‘ab initio’ since the size of the cavity is an empirical parameter entering the calculations. Theoretical considerations do not give a unique answer to the size and the shape of the solute cavity and, therefore, SCRf calculations possess significant semiempirical character [18,19]. In any event, it is useful to compare the calculated free energies of solvation with the experimental values for isolated species in order to get a feeling about the reliability of the calculated values.

In this study, we addressed the question about the stability of the phenol–TETMA complex vs. the stability of the dissociated species. We did not consider the rest of the reaction coordinate for the association that might be associated with a barrier. In any event, such a barrier is expected to be small and would have no impact on the kinetics of the dissociation.

Chandrasekhar et al. [20] performed the free energy perturbation study of methylchloride–chloride ion in aqueous solution using discrete molecule solvent representation. They demonstrated that the reaction process in its initial phase corresponding to neutral species–ion association is barrierless.

In our solvent reaction field calculations, the solute cavity was composed of interlocked spheres. Geometry optimizations with included solvent reaction field were not performed due to the computational effort associated with the lack of analytical forces. The in vacuo optimized geometries were used. Ab-initio calculations were performed using the Gaussian-94 suite of programs [17] implemented on a Silicon Graphics Power Challenge parallel computer.

The BSSE corrected interaction energies are -9.02 kcal/mol at the Hartree–Fock level and to 8.36 kcal/mol at the B3LYP level. There is some discrepancy between the HF and B3LYP calculated geometries, indicating the complexity of the intermolecular hypersurface. At the HF level, three methyl groups of the TETMA point toward the O atom (the closest O–N distance is 3.500 Å), while at the B3LYP level one methyl group points towards the O atom (CH_3 –O distance is 3.359 Å) and two towards the aromatic carbon atoms (CH_3 –C distance is 3.768 Å).

The effect of water was included on the level of solvent reaction field. The method of Miertuš et al.

[16] as implemented in Gaussian-94 was applied. In this method, the solute cavity is composed of interlocking spheres. Our calculations were at the B3LYP/6-31G(d) level, while the radii of the spheres were van der Waals radii multiplied by 1.2. The in vacuo geometries were used. A dielectric constant of ($\epsilon = 78.3$) was applied. The calculated free energy of hydration for TETMA is -53.49 kcal/mol, while the experimental value is -54.4 kcal/mol [21]. For phenol, the experimental free energy of hydration is -6.6 kcal/mol [22] while the calculated value is -4.42 kcal/mol. The agreement is surprisingly good, and gives us confidence in the calculated values for the complexes for which experimental data are not available. The calculated free energy of association is -11.06 kcal/mol. The interaction free energy seems to be too favourable, giving rise to a large association constant. One should not forget that the applied solvent reaction field method does not take into account specific interactions such as hydrogen bonds. On the other hand, solvent reaction field calculations of hydration free energies of individual species yield values that are in good agreement with experiment.

4. Conductivity measurements

If presented in the complex plane, all measured impedance spectra consist of a high-frequency arc and a low-frequency ‘tail’. The high-frequency arc is attributed to the electrical transport due to the bulk ion migration and, in parallel with that, a capacitive current due to the dielectric displacement current in the bulk electrolyte solution, as well as the capacity due to leads, contacts and other uncompensated capacitive contributions due to the cell geometry. The low-frequency tail is attributed to the resistance of transport process(es) across or in the immediate vicinity of the electrolyte/electrode interface coupled with the double-layer capacitance [23].

The electrolyte solution conductivity was determined from the measured impedance spectra in two ways. In the first, and simpler procedure, the section on the real axis between the coordinate origin and the minimum value of the imaginary part (at intermediate frequencies, i.e. at ~ 2000 Hz) was defined as the absolute electrolyte resistance. Knowing the

cell constant, this value was readily transformed into electrolyte conductivities which, in the present Letter, are given in $\Omega^{-1} \text{ cm}^{-1}$. The second way to determine the electrolyte conductivity was by fitting the high-frequency arc using the Cole–Cole expression [23]

$$Z(\omega) = \frac{R}{1 + (j\omega RC)^\alpha}, \quad (1)$$

where R is the resistance, C is the capacitance, α is a parameter related to a distribution of relaxation times, and $j = \sqrt{-1}$.

The difference between both methods of conductivity determination was $< 0.1\%$, i.e. less than the standard deviation of consecutive measurements performed on the same electrolyte system and at the same conditions ($\sigma = \pm 0.2\%$ of the average measured value).

To determine the possible effect of phenol on the conductivity of a given electrolyte solution, the following general procedure was adopted:

(a) first the conductivity of the given solution without phenol was determined as accurately as possible (average standard deviation of a set of consecutive measurements under the same conditions was $\leq \pm 0.2\%$ of the average measured value);

(b) then a water solution of phenol (usually 0.75 M) was added in steps of 1, 2, or 5 ml to the solution under consideration. During and after each phenol addition, the electrolyte solution was thoroughly stirred. After several minutes of electrolyte solution equilibration two or three consecutive impedance spectra were measured.

The pH of the solutions was carefully monitored during the experiments. No significant change in pH took place.

4.1. Diluting $(\text{CH}_3)_4\text{NCl}$ with water

The initial nominal concentration C_0 of $(\text{CH}_3)_4\text{NCl}$ was 0.0075 M. Dilution with water led to a gradual and approximately linear decrease in conductivity, but with a smaller slope than would have occurred if ideal dilution took place (compare respectively the measured points denoted by crosses and the solid line in Fig. 2). Indeed, the slope of the measured curve agrees to a certain extent with that

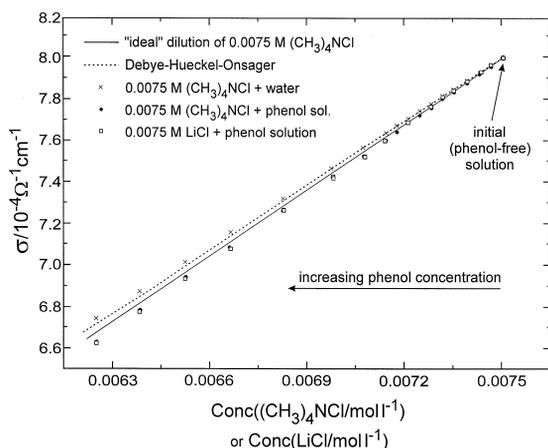


Fig. 2. Dependence of electrolyte conductivity ($\Omega^{-1} \text{ cm}^{-1}$) on its nominal concentration. The circles and squares were obtained by diluting the initial solution with a 0.75 M phenol solution. The other three curves (or points) were obtained by diluting the initial solution with pure water. For the sake of easier comparison, the measured conductivity values for the LiCl electrolyte were normalised in such a way that the initial conductivity matched the conductivity of the $(\text{CH}_3)_4\text{NCl}$ electrolyte. Note that each of the curves consists of points pertaining to two separate sets of measurements performed at the same conditions; at given resolution many of the points completely coincide, reflecting the very good reproducibility of the conductivity measurements in the present experimental configuration.

predicted by the classical Debye–Hückel–Onsager equation for a symmetrical electrolyte [24–27] (dashed line in Fig. 2):

$$\sigma \left[\Lambda_0 - (A + B) \Lambda_0 \sqrt{C} \right] C, \quad (2a)$$

where

$$A = \frac{e^2 N_A}{3\pi\eta} \sqrt{\frac{2e^2 N_A}{\varepsilon \varepsilon_0 kT}}, \quad (2b)$$

$$B = \frac{e^2 \omega}{24\pi\varepsilon \varepsilon_0 kT} \sqrt{\frac{2e^2 N_A}{\varepsilon \varepsilon_0 kT}}.$$

Here Λ_0 is the equivalent conductivity at infinite dilution, C is the electrolyte concentration, e is the absolute value of electron charge, N_A is Avogadro's number, η is the solution viscosity, ε is its dielectric constant, ε_0 is the permittivity constant (permittivity of vacuum), k is Boltzmann's constant, T is temperature and ω is a constant (for water solutions it equals 0.5859). The following parameter values were

inserted to obtain the solid line in Fig. 2: $\varepsilon = 78.3$, $T = 297 \text{ K}$, $\eta = 8.95 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ and $\Lambda_0 = 1.216 \times 10^{-2} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$. The slight deviation of the curve predicted from Eq. (2a) and the measured points (denoted by crosses) was expected because the concentration values were higher (from 0.005 to 0.0075 M) than are usually used in such comparisons (e.g., from 0.0001 to 0.001 M solutions) and where the Debye–Hückel–Onsager equation holds very well [24]. The relatively high concentration values were used primarily in order to be in the 'safe' conductivity range, i.e. about three orders of magnitude above the conductivity of distilled water and more than two orders of magnitude above the conductivity of a typical phenol solution used in the present investigation. This means that the conductivity fluctuations due to slight variation of pH, temperature, etc., were reduced as much as possible.

4.2. Diluting $(\text{CH}_3)_4\text{NCl}$ with a phenol solution

The initial nominal concentration C_0 of $(\text{CH}_3)_4\text{NCl}$ was 0.0075 M. As before, to this solution a 0.75 M phenol solution was added in steps. The conductivity of the phenol solution itself was checked. In the concentration range of interest for the present investigation, it was found to be below $10^{-5} \Omega^{-1} \text{ cm}^{-1}$, i.e. two orders of magnitude lower than that of the $(\text{CH}_3)_4\text{NCl}$ electrolyte solution. Fig. 2 shows that in the case of phenol addition, the slope of the conductivity vs. concentration curve is steeper than that predicted by the ideal dilution (compare circles with the solid line). One could try to explain this effect by a change in the average dielectric constant and/or a change in average solution viscosity which, according to Eq. (1), determine the conductivity–concentration slope. For example, it is easy to show that if the dielectric constant at the largest dilution used here decreased from 78.3 to 66 (and, at the same time, the viscosity remained constant) (Eq. (2b)) would fit very well the measured circles in Fig. 2. Knowing, however, that at the largest dilution the mole ratio between phenol and water was still only 1:250, it was hard to believe that such a large drop in average dielectric constant should occur. To check whether this reasoning was plausible, the variation of dielectric constant upon addition of phenol was measured in a separate set of measurements.

4.3. Change in dielectric constant of electrolyte solution upon addition of phenol

In these experiments, phenol was added to pure water rather than to the electrolyte. In this way we could measure directly the high frequency limit of the water capacity which is proportional to the high frequency limit of the dielectric constant. Making about 50 measurements at various concentrations gave an average high-frequency capacity value of $(188.2 \pm 1.5) \times 10^{-10}$ F (the capacitance of the measurement cell itself was $\sim 1.5 \times 10^{-12}$ F). On the other hand, the standard deviation of these capacity measurements, determined from a set of 15 consecutive measurements at the same conditions, was 0.99×10^{-10} F. If these data are presented in terms of dielectric constant values, the maximum possible drop is 1.3, i.e. from 78.3 to 77.0 (taking into account the standard deviation of capacity measurements, however, it is clear that up to 67% of this drop may be attributed to the error of dielectric constant measurement). These results confirm our expectations that small amounts of phenol (equal or less than 1:250 in mole ratio with respect to water) have a negligible effect on the average dielectric constant of the solution.

4.4. Change in electrolyte solution viscosity upon addition of a phenol solution

When adding phenol to a water solution, the viscosity is expected to increase. Again, due to a very small mole ratio between phenol and water (1:250), this increase should be negligible under the present experimental conditions. In any case, it is easy to show that even if the change in viscosity were considerable, it could not explain the observed increase in the slope of the curve (see Fig. 2). Namely, simulations using Eq. (1) show that any increase in viscosity would lead to a decrease of the curves slope – an effect exactly opposite to the measured one.

4.5. Diluting LiCl with a phenol solution

If instead of $(\text{CH}_3)_4\text{NCl}$ a 0.0075 M LiCl salt is used and phenol is added in the same way as before, a curve is obtained that matches that obtained with the $(\text{CH}_3)_4\text{NCl}$ electrolyte well (for the sake of

easier comparison, all measured LiCl conductivity values were multiplied by an appropriate constant so that the initial conductivity was the same as for the $(\text{CH}_3)_4\text{NCl}$ electrolyte). This result might indicate that the Li^+ ion interacts with phenol in a similar way as the $(\text{CH}_3)_4\text{N}^+$ ion. At least in vacuo, it has been shown by mass spectrometric studies that the Li^+ ion forms a stable complex with benzene with a binding enthalpy of -38 kcal [2]. It is expected that the complex with phenol is even more stable. One may speculate that the Li^+ -phenol complex is also stable in aqueous solution.

5. Discussion

Both theory and the experiment are giving evidence for stable complexes between the tetramethylammonium ion and phenol in aqueous solution.

A critical component of the DFT method applied in the present case is the treatment of the aqueous environment. We used the solvent reaction field approach. On one hand, one may argue that specific interactions, such as hydrogen bonds, are omitted in this way. On the other hand, the inclusion of the solvent reaction field by the method of Miertuš et al. [16] at the B3LYP/6-31G(d) level nicely reproduced the experimental free energies of hydration of the individual species for which the experimental data are available. It is worth emphasising that the experimental free energies of hydration of the TETMA ion are subject to significant experimental uncertainty. In the early works [28,29], a value of -46.5 kcal/mol is reported. However, Aue et al. [21] report an experimental value of -54.4 kcal/mol. The calculated free energy for association of phenol and tetramethylammonium ion predicts that the process is thermodynamically favourable. Please note that ab-initio calculations predict the complex in aqueous solutions to be too stable.

Indeed, measurements of conductivity changes upon the addition of a phenol solution into a solution containing $(\text{CH}_3)_4\text{NCl}$ indicate that phenol does form complexes with TETMA ion. However, the relative decrease in conductivity due to the presumable complex formation is small, i.e. at most 2%. If all TETMA ions formed complexes with phenol, and the mobility of such complexes was zero (one of the

limiting cases), then a total conductivity decrease of 37% would be expected. One should bear in mind that the TETMA ion per se is bulky and it is not expected that its complex with phenol will exhibit a drastically decreased mobility; by no means is its mobility expected to be zero (vide infra). There are two possible interpretations of the measurements. The TETMA ion–phenol can form relatively weak complexes. This does not agree with the calculated DFT binding free energies. The second possibility is that the mobility (equivalent conductivity) of the complex is not significantly lower than the mobility of the TETMA ion per se.

Since no experimental data on the conductivity of the TETMA–phenol complex are available, one has to consider the conductivities of related species with covalent bonds between TETMA and aromatic rings. Benzyltrimethyl–ammonium ion is a good candidate for such a comparison. Inspection of experimental values for equivalent ionic conductivities [11] reveals that the equivalent ionic conductivity of the tetramethylammonium ion and benzyltrimethyl–ammonium are 44.9×10^{-4} and $34.6 \times 10^{-4} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$, respectively. Since the latter species is structurally closely related to the TETMA–phenol complex, one may conclude that the second interpretation of the measurements should be considered. If one assumes that the mobility of the complex equals the mobility of the benzyltrimethylammonium ion, then a rough estimate is that the total decrease of conductivity of the TETMA–phenol solution is 11% in the case of total association. In our case the reduction of conductivity is 2%. Therefore, our estimate is that $\sim 20\%$ of all TETMA ions form complexes.

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