

PROTON-TRANSFER IN 1,1,3,3-TETRAMETHYL GUANIDINE BY MEANS OF ULTRASONIC RELAXATION SPECTROSCOPY AND MOLECULAR ORBITAL CALCULATIONS

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ABSTRACT

In this study we attempt to examine the mechanism of the protonation reaction taking place in aqueous solutions of 1,1,3,3-Tetramethylguanidine (TMG). This can be achieved by the utilization of an ultrasonic relaxation method as well as vibration spectroscopy and some molecular orbital calculations. Various aqueous solutions of TMG in the range of 0.1 to 1.0 mole fraction were prepared. We examine the frequency and temperature dependence of the relaxation of the process using the Pulse-Echo method in the frequency range 1 – 50 MHz as well as eliminate any suspicions of existence of some byproducts that may form in the solutions. The Pulse-Echo method is selected here due to its accuracy in the determination of the properties of the guanidine, especially in this frequency region. Raman spectroscopy and the molecular orbital calculations were adequate enough to alleviate any theories of any other reactions taking place in the system of solutions.

INTRODUCTION

Guanidines are a group of organic compounds sharing a common functional group with the general structure (R1R2N)(R3R4N)C=N-R5. The central bond within this group is that of an imine, and the group is related structurally to amidines and ureas. An example of a guanidine is the 1,1,3,3-Tetramethylguanidine (TMG) with the molecular formula of $[(CH_3)_2N]_2C=NH$. This guanidine is a strong base and the study of its protonation reaction is of great significance due to its use in an abundance of applications in ionic liquids, and is more specifically used in the absorption of CO₂.

An inexpensive, non-destructive and accurate method of studying the mechanism and the properties of the protonation reaction of TMG is the ultrasonic relaxation spectroscopy. Ultrasonic techniques belong to the stationary relaxation techniques and their use depends on the frequency range of interest. These techniques cover the 10⁴ to 10¹⁰ Hz frequency region, which means that one may perform relaxation times measurements in a wide time scale, namely between 10⁻⁵ to 10⁻¹¹ seconds. These very short times are difficult to be measured by other transient techniques and thus acoustic techniques have been proved a powerful and less expensive tool in describing the dynamic picture of a molecular system. Furthermore, an additional advantage of ultrasonic techniques is that there are no restrictions on the type of processes that can be studied.

Despite the large amount of studies concerning the structure and dynamics of aqueous solutions of non-electrolytes by ultrasonic methods, much less attention has been paid to the aqueous solutions of guanidine derivatives and to the interpretation of the underlying absorption mechanism.

The purpose of our study is to provide comprehensive understanding on the structure and dynamics of the aqueous solutions on non-electrolytes by combining vibrational and ultrasonic spectroscopies. We report on the proton transfer reaction occurring in aqueous TMG solutions by measuring ultrasonic absorption and velocity as a function of concentration and temperature. The results are discussed and compared with analogous aqueous solutions of alcohols. The possibility

of formation of other product during hydrolysis of TMG has been elucidated using Raman spectroscopic data.

EXPERIMENTAL

Materials

Liquid 1,1,3,3 tetramethyl guanidine (TMG) corresponding to molecular formula $(\text{CH}_3)_2\text{NC(=NH)N(CH}_3)_2$ of high purity (99.9%) was obtained from Aldrich. TMG is an organic colorless liquid. This amine is a strong base with a higher pKa than typical amines. No further purification was attempted. Solutions of TMG dissolved in triple distilled water were prepared gravimetrically by using standard procedures and correspond to the concentrations 2×10^{-5} , 2×10^{-4} , 2×10^{-3} , 2×10^{-2} , 2×10^{-1} , 0.80, 2.00, 3.48, 5.08, 5.99, 6.58, 6.99, 7.30, 7.53, 7.72, 7.87 and 7.97 M. Caution must be taken in the handling of TMG because eye damage and/or blindness may occur in case of contact with the eyes. It is interesting experimental observation was that when TMG was cooled then the supercooled liquid became increasingly viscous, while fast quenching resulted in a glassy material.

Ultrasonic relaxation spectroscopy - Pulse-Echo technique

Ultrasonic absorption measurements were performed in the 1 to 50 MHz frequency range utilizing the pulse-echo technique where the amplitude of the pulse-modulated ultrasonic wave is measured after passing the liquid sample. From the exponential decrease of the echo's amplitude one is able to calculate the corresponding ultrasonic attenuation coefficient. The same transducer (Olympus V111, 10 MHz) was used as transmitting and receiving transducer for the absorption measurements. Pulses were generated from a frequency generator (TTi, TGP3151) in a wide frequency-range. The pulse triggering and the detection was performed by a digital oscilloscope (Tektronix, TBS 1202B). The liquid absorption cell used for the measurements was temperature-controlled by means of an external circulation system. The relative measurement error for absorption is estimated to be of the order of $\pm 5\%$, while temperature was controlled to within $\pm 0.1^\circ\text{C}$. In order to measure the ultrasonic sound velocities the same absorption cell was used at a frequency of 5 MHz by employing the overlapping pulse-echo method for all concentrations and temperatures studied. The maximum error for velocity measurements was estimated to be less than $\pm 1.0\%$.

Raman Spectroscopy

A detailed description of the Raman set up and the procedures necessary for acquiring accurate polarized and depolarized Raman spectroscopic measurements in the liquid state have been reported previously^[1-5]. In brief, Raman spectra are excited by the 532.0 nm linearly polarized laser line (Spectra-Physics Excelsior) in a 90° scattering geometry. The power level at the sample was fixed at 40 mW. All spectra were recorded with a spectral resolution set at 1.5 cm^{-1} . Both polarization geometries were employed, namely the vertical-vertical (VV) and horizontal-vertical (HV) configurations. Possible monochromator's drift was calibrated using the reference line of a Neon lamp, while the depolarization ratio accuracy was checked by a CCl_4 reference sample.

Quantum chemical molecular orbital calculations

Structure modeling and calculation of the vibrational spectroscopic properties were performed using the Gaussian 09 series of programs^[6]. As input, we used the optimized geometries after minimization of the corresponding electronic energy as a function of the geometry under tight optimization convergence criteria using the MP2 levels with the 6-311++G(d,p) basis set. All calculations were carried out with the use of the DFT/B3LYP^[7,8] functional with the 6-311++G(d,p)

basis sets with polarization functions and diffuse orbitals. The vibrational frequencies for each normal mode were obtained following analogous methodology^[9]. DFT frequency calculations were performed not only in the gas phase, but also in the presence of water as solvent, which behaves as homogeneous and isotropic and characterized by the corresponding dielectric properties. All calculations were performed without adjusting force constants and the wavenumber values were corrected with the corresponding scaling factor. The level of modeling used has proved to be satisfactory to describe the nitrogen containing compounds.

RESULTS AND DISCUSSION

Structural properties – vibrational modes

Several mechanisms may account for the structure of the TMG amine when dissolved in water. The first corresponds to the proton transfer reaction, while two different products may be formed from the hydrolysis of TMG. The first hydrolysis reaction involves the production of 1,1 dimethyl urea and dimethyl amine as products. The second possible hydrolysis reaction involves the formation of tetramethyl urea and ammonia. In order to determine which mechanism takes place during the dilution of TMG, we recorded the Raman spectra of all solutions corresponding to mole fraction from 0.1 to 1 with steps of 0.1 covering a wide concentration range from dilute to dense solutions.

We compared the experimental polarized (VV) Raman spectrum of pure TMG with the corresponding calculated spectrum in the vapor phase. It seems that all bands coincide in frequency, while differ in the relative intensities in the low-frequency region. The comparison reveals that the theoretical model used predicts successfully the experimental Raman spectrum despite the fact that the calculation is performed in the vapor state. Complete and accurate assignment of the fingerprint region is difficult to perform without deuteration studies.

We have used this prosperous model to elucidate the mechanism of TMG dilution in water. We compared in **Fig. 1** the experimental Raman spectrum of aqueous TMG solution with 0.1 mole fraction of amine (highly diluted region) with that calculated using water as solvent. Also, in this case the similarity is almost perfect. The differences are in the low-frequency intensities and the presence of a broad spectral envelop in the high-frequency region, which is absent from the theoretically predicted spectrum. In the same figure is also shown the experimental polarized (VV) Raman spectrum of water recorded at ambient conditions. It is evident that the observed spectral envelop in the high-frequencies exhibited by the 0.1 mole fraction aqueous solution of TMG is attributed to water vibrational bands. The spectrum of the solution seems to be a superposition of the calculated and pure water spectra. In order to examine the possibility of formation of Tetramethylurea and/or 1,1-Dimethylurea as products, we compared the calculated Raman spectra of both possible products with the experimental spectrum of the aqueous solution corresponding to x=0.1 mole fraction (3.48 M) and the comparison reveals that mechanism other than proton transfer is questionable.

Dynamic properties – Low-concentration region

No ultrasonic relaxation was observed for water in the 1-50 MHz frequency range and for all temperatures studied. In **Fig. 2** we present representative results of the absorption coefficients divided by the square of the frequency, a/f^2 of aqueous TMG solutions at 25°C from 2×10^{-5} to 2 M covering a wide range of concentrations. The a/f^2 measurements were found frequency dependent and have been analysed by a Debye-type equation as:

$$\frac{a}{f^2} = \frac{A}{1 + \left(\frac{f}{f_r}\right)^2} + B \quad (1)$$

where α and A represent the ultrasound absorption coefficient and the amplitude of relaxation, respectively.

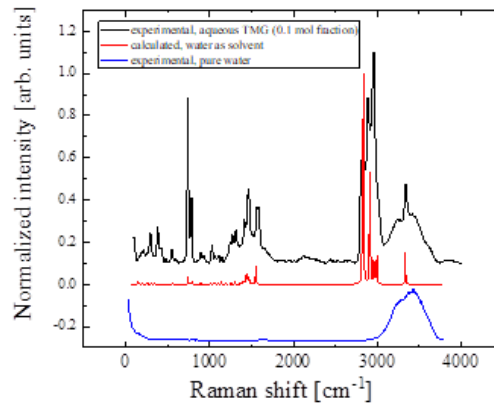


Figure 1. Comparison of the experimental Raman spectrum of aqueous solution of TMG with 0.1 mole fraction (3.48 M) with the calculated one and with the one of pure water.

The constant B accounts for the background absorption from other sources, such as vibrational relaxation and/or viscothermal absorption and f_r is the characteristic relaxation frequency. From the adequate goodness of fit we conclude that only one Debye-type relaxation is observed in the TMG aqueous solutions. From the concentration dependency of the ultrasound absorption coefficient it seems that the observed single relaxation is associated to the proton transfer reaction. **Figs. 3(a) and (b)** show the concentration-dependence of the relaxation frequency and amplitude, respectively. In both cases a clear monotonous increase is observed with increasing the concentration of the amine in the solutions. The almost perfect linear dependency further supports the assignment of the ultrasonic relaxation to the proton transfer reaction. The experimental ultrasonic velocity is also shown in **Fig. 3(c)**. The sound velocity is a key thermo-physical property related to the dynamic response of the condense phase. The results reveal that sound velocity remains almost constant and increases rapidly above 10^{-1} M indicating alterations in the network rigidity. In the water-rich region, the hydrogen bonded network of water is not affected by the presence of the TMG hydrophobicity, which is considered to be small.

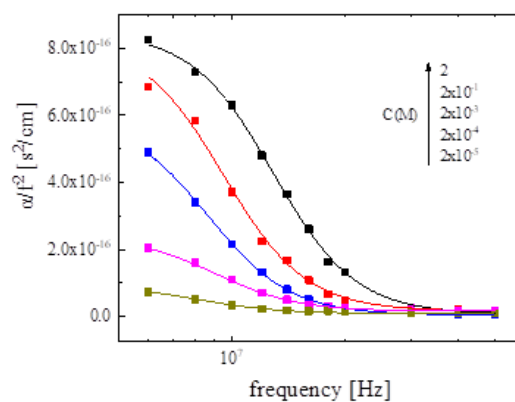


Figure 2. Fitted curves of a/f^2 vs f at 25°C in various concentrations of aqueous solutions of TMG.

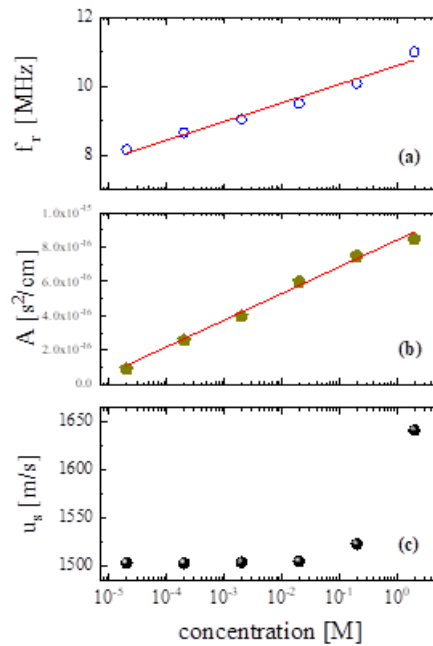


Figure 3. a) Concentration dependence of the relaxation frequency, b) Concentration dependence of the relaxation amplitude and c) Concentration dependence of the sound speed.

Representative ultrasonic absorption spectra as a function of temperature are presented in Fig. 4 for a solution with concentration 0.8M. The results reveal a reduction in the α/f^2 ratio as the ultrasound frequency is increased in the temperature range studied and also in this case are typical of a single Debye-type relaxation. The characteristic relaxation frequency was estimated using the same fitting procedure as before and is related to the thermodynamic parameters of relaxation through the equation:

$$f_r = \left(\frac{k_B T}{2\pi h} \right) \exp\left(-\frac{\Delta H^*}{RT}\right) \exp\left(\frac{\Delta S^*}{R}\right) \quad (2)$$

where k_B and h are the Boltzmann and Planck constants, respectively. ΔH^* is the activation enthalpy and ΔS^* is the corresponding activation entropy.

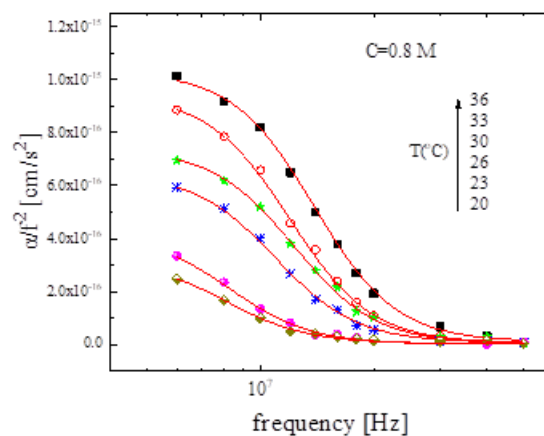


Figure 4. Fitted curves of the ultrasonic absorption spectra as a function of temperature at a fixed concentration

In Fig. 5 is shown the graph of $\ln(f_r/T)$ versus $1/T$. The results follow a clear linear dependency implying the presence of a single relaxation process. The activation enthalpy ΔH^* is obtained from the slope of this graph and found equal to $\Delta H^* = 5.56 \pm 0.34$ kcal/mol, which seems to be reasonable for hydrogen-bond formation.

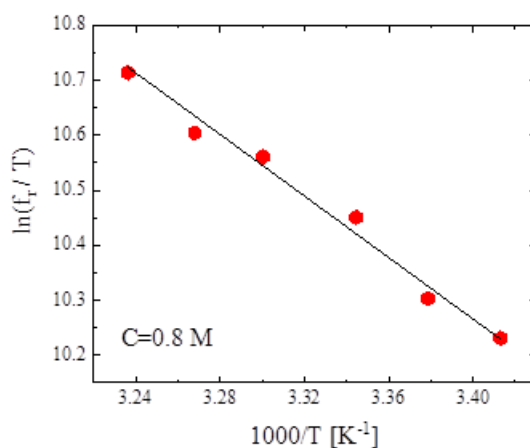


Figure 5. Arrhenius plot of $\ln(f_r/T)$ versus $1/T$.

CONCLUSIONS

In this work, the combination of the vibrational and ultrasonic data allowed us to determine the nature of the mechanism of the protonation reaction of TMG in aqueous solutions. Through Raman spectroscopy and molecular orbital calculations, we were able to obtain the experimental and theoretical vibrational Raman spectra that were in a very good agreement with each other. By doing this, we are confident that there is no existence of any by-product in any of our solutions. Moving to the ultrasonic studies, we were able to identify a single relaxation process through the ultrasonic intensities and linearity of the relaxation frequency and the amplitude. Furthermore, the temperature dependent measurements show a linear dependency when plotted in an Arrhenius diagram, and therefore we can calculate the activation enthalpy, from the slope, to be $\Delta H^* = 5.56 \pm 0.34$ kcal/mol. This result leads us to be more certain for hydrogen-bonding formation.

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