ANOMALOUS STATE OF ICE

SHUI-YIN LO*

Anomalous state of ice, which is a novel stable structures made from water molecules, can be induced to form under the action of ions in very dilute solutions, perhaps from a similar physical mechanism that forms ice VI. These stable structures change the UV *transmission* characteristic of water. Different *structures* formed from different ions are shown to have similar UV transmission characteristics. These structures can be filtered, concentrated and photographed using a transmission electron-microscope. A dipole–dipole interaction model is constructed to suggest an explanation of the elongated shape of these structures.

1. Introduction

It is well known that water molecules form stable rigid structures: for example, ice VI at room temperature and at high pressure (>7 kB).[1] Generally, such a high pressure does not occur naturally on Earth. However, we wish to point out that such a high pressure could exist between an ion and its nearby water molecules due to the electrostatic attraction between the charge of an ion and the electric dipole moments of a water molecule. Anomalous state of ice which are stable rigid structures of water molecules similar to ice VI can be grown in water at room temperature and normal pressure provided that suitable dilution of ions in water is performed.

2. Growing Structures Around Ions in Very Dilute Solution

Positively or negatively charged ions in aqueous solutions attract water molecules which have electric dipole moments p that can be expressed as $p = \eta ed = 2.45$ debyes, with e = charge of electron, d = size of water molecule = 0.278 nm and η = scale factor = 0.1837. The electric potential energy, U, experienced by a water molecule at a distance r from the ion is $U = - p \cdot E$ where E is the electric field

*Visiting Associate, Department of Chemistry, California Institute of Technology, Pasadena, CA 91107, USA.

exerted by the ion on the water molecule and is given by

$$E = -\frac{e}{[4\pi\varepsilon r^2]\hat{r}} \tag{2.1}$$

with ε = dielectric constant of water = 80. The pressure, P, experienced by the water molecule is equal to the energy density:

$$P \approx \frac{U}{d^3} = \frac{\eta e^2}{4\pi\varepsilon r d^2}. \tag{2.2}$$

The pressure is inversely proportional to the square of the distance between the ion and water molecule which is a characteristic of coulomb force. The pressure is smaller by a factor of e as compared with vacuum because of the dielectric property of water. Numerically, it is $P = 0.61$ kB/s^2, where $s = r/d$ is the distance scaled in units of water molecule size. However if the next layer of water molecules around an ion are packed in a regular, spherical symmetric rigid fashion, the pressure experienced by the water molecule immediately outside this layer will be boosted by a factor of $\varepsilon = 80$. This is because the electric field determined from Gauss law $\oint \mathbf{E} \cdot ds = Q/\varepsilon_0$ is given by the total charge Q enclosed by a closed surface; and the surface is chosen to include the ion and the next layer of water molecules completely. The polarized positive and negative charge of any water molecule is all inside the same closed surface and they cancel out one another. The total charge Q is that of the ion and does not contain polarization from water molecules. So the pressure exerted by an ion on the sth layer of orderly arranged water molecules is in fact boosted to $P = 71.8$ kB/s^2. For the second layer ($s = 2$) of water molecules around an ion, the pressure is 18 kB and the pressure decreases to 8 kB when $s = 3$. If one checks on the phase diagram of water, water turns to ice VI at room temperature at pressure around 7 kB.

With a large pressure arising from a regular structure, one may expect that the water molecules surrounding an ion will turn into ice VI. It is, however, not the ordinary ice VI where the unit cell has a translational invariance. One expects that the crystalline structured water surrounding the ion would have special symmetry due to the spherical symmetrical nature of pressure. There is no study on what properties a spherical symmetric ice crystal should have. The unit cell probably is not rectangular. For lack of a better reliable alternative, it is assumed that the spherical symmetric icy structures surrounding ions have similar properties as that of ordinary ice VI and ice VII. We will call it I_E structure indicating that it is an icy structure formed under the effect of an electric field.

The I_E structure formed around ions is influenced by the movement of ions in water. When two similar charged ions come close together, the pressure on water molecules between them decreases and the I_E structure previously formed will melt. As the ions move away from each other, the pressure builds, and the I_E structure starts to grow again. Let the destruction rate of the I_E structure due to collision be RD and the growth rate of the I_E structure be R_G. The destruction rate is given by the inverse of collision time t_c: $R_D = 1/t_c$. When ions move in a random fashion in

a solution, the collision time is $t_c = k_i^2 \Delta t$, where k_i is the average number of water molecules between two ions and Δt is the collision time between an ion and water molecule. The growth rate R_G is the growth speed v_g of the I_E structure divided by the size of the structure α_c. Therefore the condition for the existence of stable I_E structures in a very dilute solution is: growth rate R_G greater than destruction rate R_D or

$$k_i \gg \left[\frac{a_c}{v_g \Delta t}\right]^{1/2}$$

(2.3)

The growth speed v_g of ordinary ice is well-known to be a function of super-cooling temperature.[1] It ranges from 10^{-4} cm/sec to 10 cm/sec depending on how far (10^{-2}°C to 10°C) the temperature is from the phase transition point at 0°C. In our case the growth of I_E structures comes from the deviation in pressure rather than in temperature from the phase transition point. Let us take the fast growth rate $v_g = 3$ cm/sec, $\alpha_c \sim 3d$ and $\Delta t \sim 10^{-12}$ sec, then the average number of water molecules between ions k_i has to be greater than 167. Or the ratio of density of ions n_1 to that of water molecules has to be smaller than $n_1/n_0 < 2.2 \times 10^{-7}$ which is about 10^{-5} molar concentration and a very dilute solution indeed before there are stable I_E structures.
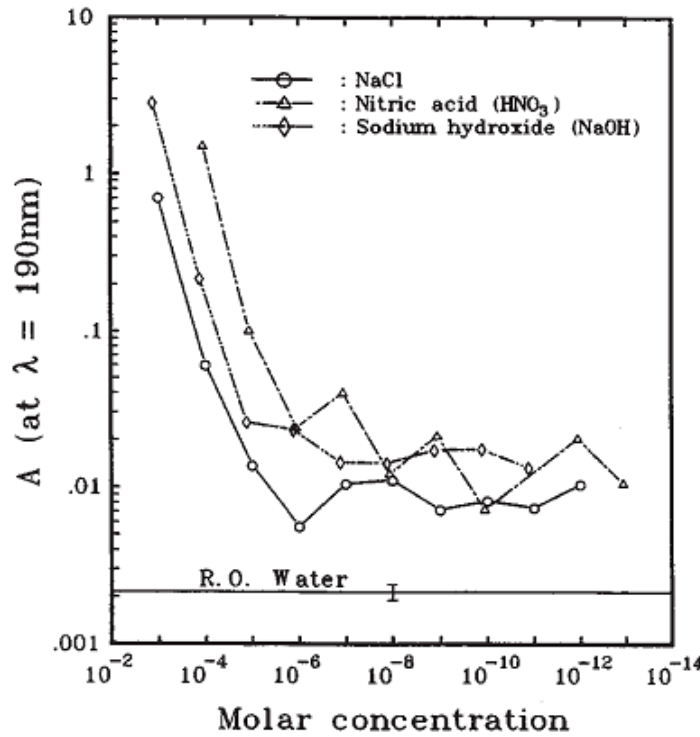
(a)

Fig. 1. (a) UV absorbance (A) measurement at wavelength $\lambda = 190$ nm for three very dilute solutions: NaCl, NaOH, HNO$_3$ at different molar concentrations. The control sample is pure water (RO water, bottom line). (b) UV transmission measurement in the interval of wavelength from $\lambda = 190$ nm to 250 nm for very dilute solutions of NaCl with molar concentrations of 10^{-5} (Y3), 10^{-6} (Y4), ...10^{-12} (Y10) from top to bottom. (c) UV transmission measurement for very dilute solutions of HNO$_3$ with N2 (molar concentration 1.15×10^{-5}M) and N6 (2.1×10^{-11}M), and NaOH with Na2 (1.32×10^{-3} M) and Na10) (1.32×10^{-11} M).
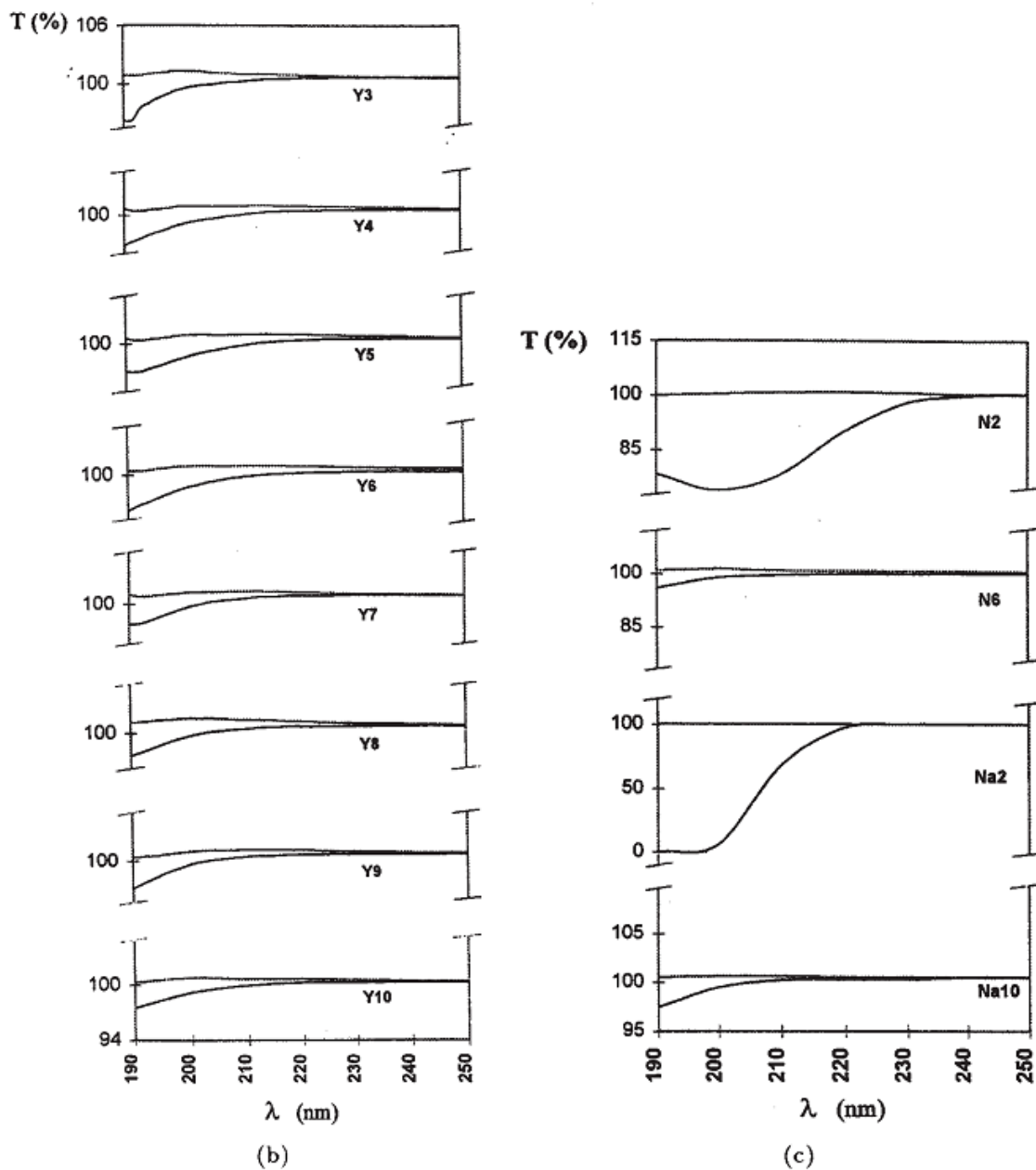
Fig. 1. (*Continued*)

3. UV Transmission Measurement

Evidence for I_E structures shows up easily in UV transmission measurement. The standard method for preparing a very dilute solution is to dissolve a small amount of salt (NaCl), acid (HNO_3), or base (NaOH) in pure water, then dilute it one part to ten parts of pure water.2 Shake the solution and dilute again one part to ten parts of pure water. Repeat this many times. The solution is measured for UV transmission via a dual beam Perkin-Elmer Lambda 2S machine with a standard reference cell filled with pure water. The absorbance readings from Lambda 2S, which also include effects from scattering as well as absorption of UV light, are

displayed in Fig. 1(a) for four solutions: sodium chloride NaCl, sodium hydroxide NaOH, and nitric acid HNO_3 and pure water with molar concentration ranging from 10^{-3} to 10^{-13}. There is clearly a drop of absorbance as molar concentration decrease. Then starting at molar concentration 10^{-5} to 10^{-7} they all fluctuate in the order of 10^{-2}, regardless of their origin. We show selectively a few UV transmission measurements for these types of solutions in the range of wave length λ = 190 nm to 250 nm in Figs. 1(b) and (c). There is no qualitative difference in the spectrum for various very dilute solutions (<10^{-7} M) made up from different salts, acids, or base. The UV transmission characteristic of these very dilute solutions is significantly different from the dilute solution when $n_i/n_0 > 10^{-7}$ or molar concentration > 10^{-5}. It is important in the experimental procedure that we carefully wash the quartz cell to get rid of any I_E structures each time a measurement is made. A clean quartz cell with pure water is verified by a flat UV transmission flat curve from the Lambda 2 machine. This is done each time prior to the next measurement.

We interpret these results as follows: As solutions become very dilute, I_E structures are formed from water molecules around ions. These water molecules are formed under strong electric field, which is 2×10^6 V/m at three water molecules distance from ions. Hence water molecules in I_E structures are expected to maintain the alignment of their dipole moments. The effective dipole moment of I_E structure is negative towards a positive ion side and positive on the side opposite from the ion. Furthermore, the electric field has spherical symmetry. This condition is quite different from ice VI formed under high pressure which has translational invariance. Unit cell of ice VI is tetragonal and can be repeated in all directions indefinitely. No one so far has constructed a crystal with a spherical symmetry. Hence not much is known about a spherical symmetric crystal or any non-translational invariant unit cell.

The I_E structures are first formed around ions in the solution and do not occur anywhere else. We could generate these structures by breaking them up with shaking. The spherical symmetric I_E structures will break up into many small pieces. These small pieces have electric dipole moment which generate a strong electric field at the poles to attract nearby water molecules to form a bigger piece. These bigger pieces are magnet like except they have an electrical dipole and not a magnetic dipole. They exist independent of ions. They can be broken into smaller pieces and grow bigger. Therefore, as the solution is diluted further from molar concentration 10^{-7} to 10^{-13}, I_E structures remain undiminished by dilution many many times. Since shaking, breaking and then growing of I_E are random, we do see a random spread of UV absorbance around 10^{-2} at λ = 190 nm for various very dilute solutions as shown in Fig. 1(a). There are great similarity among very dilute solutions of HNO_3, NaOH, and NaCl with different molar concentration and having I_E structures. In Fig. 1(c), the dilute solution N2 of HNO_3 (1.15×10^{-5} M) looks very different from both of the dilute solution NaOH (2.5×10^{-5} M) and the very dilute solution nitric acid (2.1×10^{-11} M) because UV transmission of N2 is still a characteristic of nitric acid.
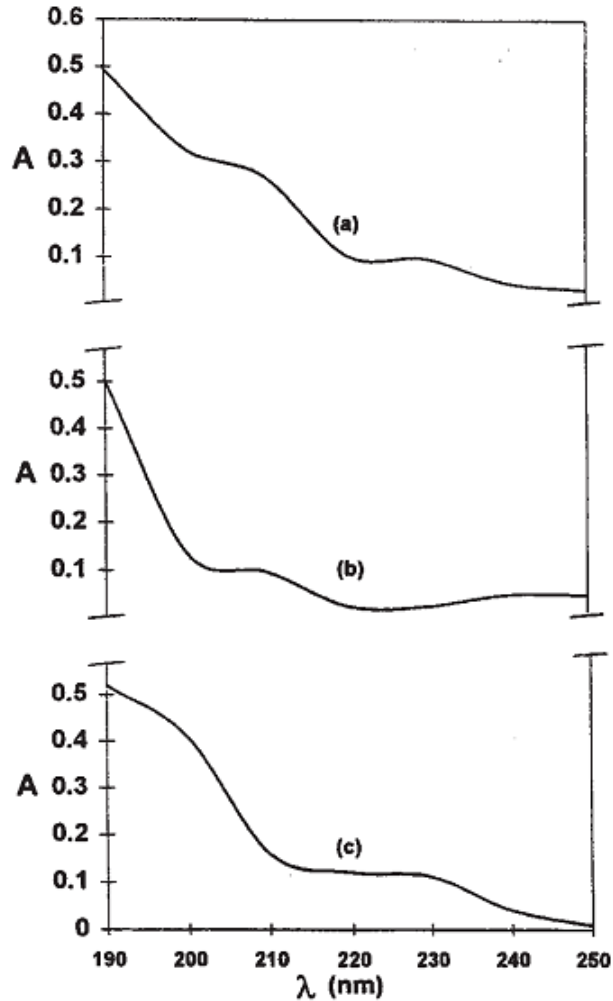
Fig. 2. The UV absorbance for a concentrate I_E structured water (a) before low pressure distillation, (b) evaporated solution and (c) residue solution.

In order to further test the idea of I_E structure, we search for a way to increase the I_E structures in the very dilute solution. In our dipole model, I_E structures created by ions cannot be big. The electric dipoles of the I_E structures on the right hand side of a positively charged ion have the induced charges in the order of negative, positive, negative, positive etc. with polarization vector pointing to the left while the electric dipoles of I_E structure on the left hand side of a positive-charged ion will have exactly the opposite polarization. Hence, the total electric dipole around an ion will tend to cancel out. Less and less I_E structure can grow away from the ion because of diminishing electric field. However for very dilute solutions with mostly I_E structures and very little ions (say $n_i/n_0 < 10^{-11}$), we introduce some dielectric material which does not ionize but has an uneven electronic distribution outside. Then I_E structures can grow outside the dielectric material with polarization lining up on both sides of the molecules. The electric dipole moments of the total I_E structure add up and there is no diminishing of the electric field at the boundary of the I_E structures. So I_E structures can easily grow bigger. For this to occur, we have experimented by introducing an dielectric material with high boiling point (~ 350°C) slowly in the very dilute solution to about several parts per million.

And we see a much stronger UV absorbance as well as many more rod-like structures in the electron microscope pictures.

Since the dielectric material having a high boiling point (350°C) and does not evaporate with water, we have used a low pressure rotary evaporator and boil the solution at 67°C. The evaporated and condensed solution has similar UV transmission characteristic as shown in Fig. 2. This strongly suggests the increase of the UV absorbance is due to an increase in I_E structures and not due to impurity such as the dielectric material that we add.

4. Electron Microscope Pictures of I_E Structures

The direct evidence for existence of these stable I_E structures comes from pictures taken with the electron microscope. The very dilute solution with I_E structures is filtered through a 0.1 μm filter paper and then is sputter coated with carbon. The carbon coated filter paper is dissolved in boiling chloroform for twenty minutes. Water and I_E structure will be dissolved away and only carbon skeletons remain. Hitachi transmission microscope H600A is used to take the pictures. The X-ray emitted by the striking electron beam is also examined. If there is any impurity such as solid salt or biological entity, a characteristic X-ray of their constituent atoms by atomic excitation will be emitted. No such characteristic X-rays are seen. Hence it is concluded that the skeleton pictures are not from impurities in the water or biological specimen such as bacteria or virus. The pictures are consistent with the hypothesis that the I_E structures are made up of water molecules alone. Some of the typical pictures are shown in Fig. 3.[3] They are from very dilute solutions of sodium chloride with small and large amount of UV absorbance. For control, we also treat pure water (reverse osmosis water from Millipore machine) the same way; we see none of these structures. Since these structures are of micron size, they can be observed by ordinary optical microscope with some patience also.

5. Dipole-Dipole Interaction Square Lattice Model

In order to understanding the rod-like structures as seen by the electron microscope, we propose the following mechanism. After the I_E structures are created, broken and then grow to larger size, they have larger electric dipole moments. The electrostatic forces between any two adjacent pieces is huge. They either join each other head to tail or side by side. If they lie side by side, their electric dipole moment will be opposite each other to obtain the lowest energy states. The circular sizes of the order of 100 nm seen inside the rod-like structures are assumed to be electric dipoles. Let us assume they are of equal size and have the same amount of electric dipole moment p. The interaction between any two dipoles i and j is given by dipole-dipole interaction.

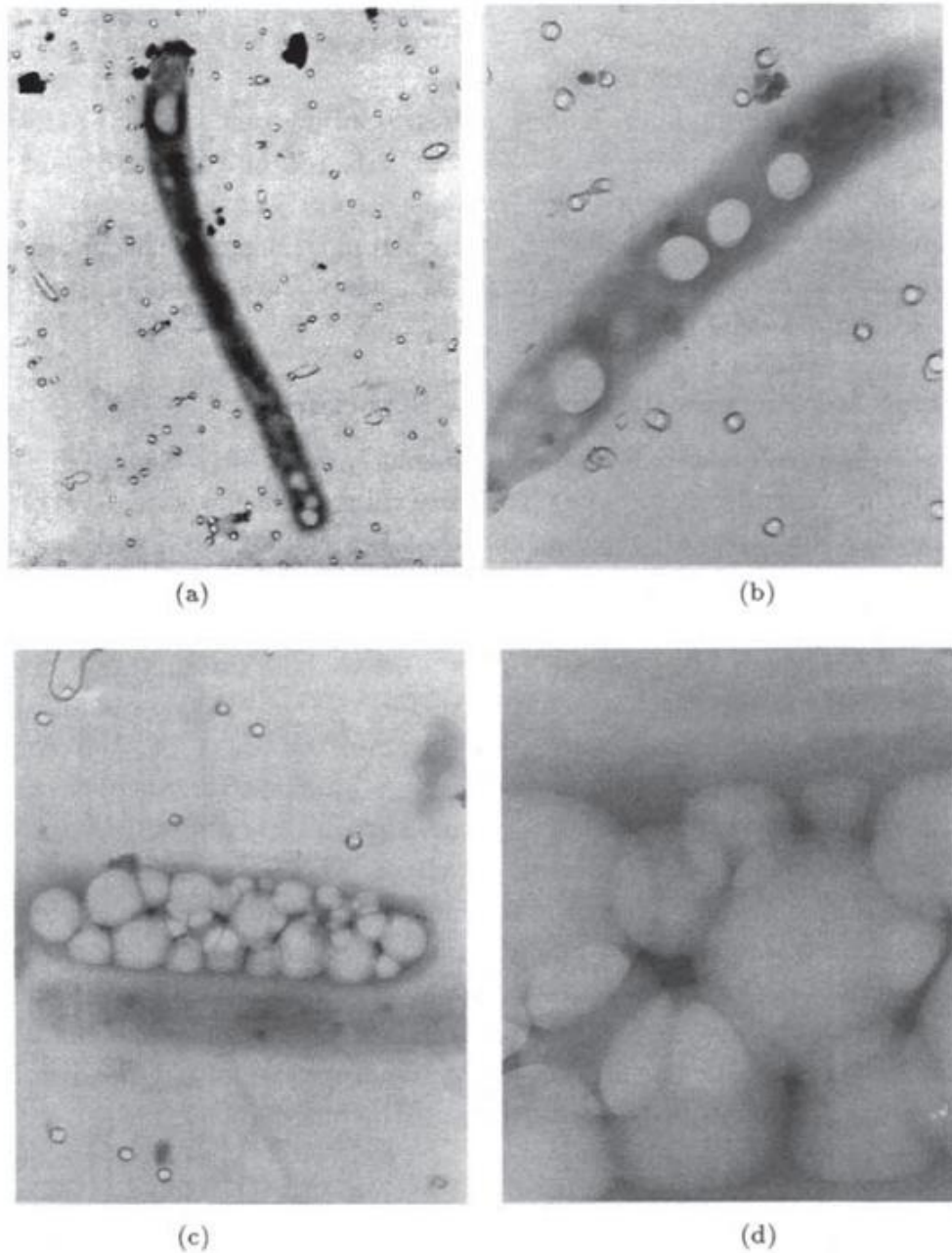$$U_{ij} = \frac{p_i \cdot p_j - (p_i \cdot \hat{n})(p_j \cdot \hat{n})}{r_{ij}^3} \tag{5.1}$$

Fig. 3. Transmission electron microscope photographs of I_E structures. (a) & (b) From NaCl (10^{-11} M) solution with UV absorbance $A = 0.0132$ at $\lambda = 190$ nm, small circles are from filter hole of 0.1 μm for all photographs. Magnification $\times 10,000$ for (a) and $\times 25,000$ for (b). (c) From concentrated NaCl solution with more I_E structures obtained from adding small amount of dielectric material, the UV absorbance being $A = 0.795$ at $\lambda = 190$ nm. Magnification $\times 20,000$. (d) A magnification of $\times 80,000$ of the middle part of the I_E structure in (c). (e) Photographs of I_E structures obtained in the way as that of (c). (f) A magnification of $\times 80,000$ of the middle part of the upper I_E structures in (e).

where r_{ij} is the distance between dipole p_i and p_j and $\hat{n}$ is the unit vector of r_{ij}. The total interaction energy of N dipoles is

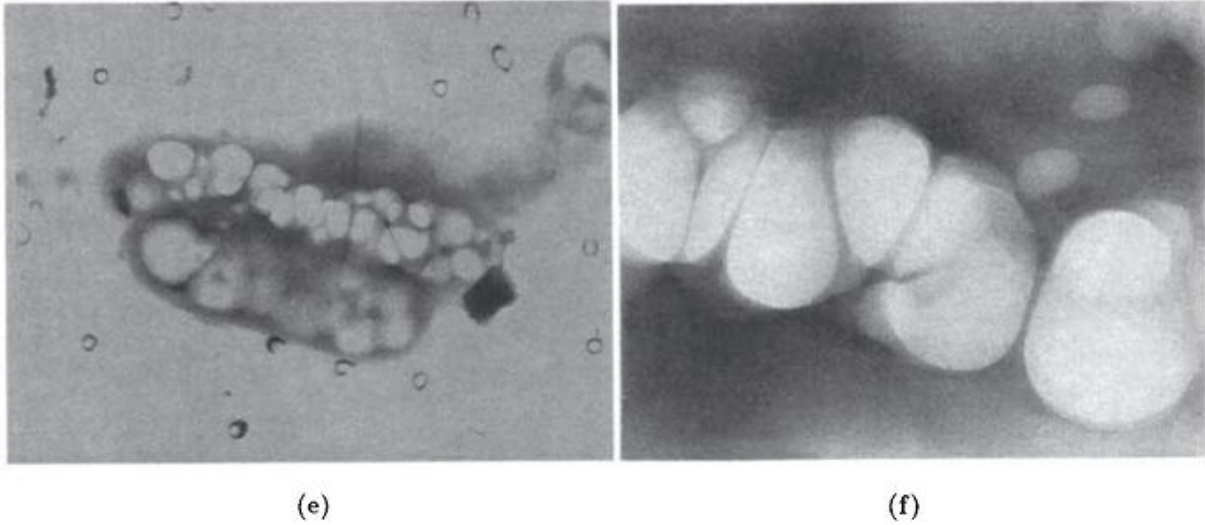$$U = \sum_{i,j}^{\Sigma} U_{ij} \cdot \tag{5.2}$$

(e) (f)

Fig. 3. (*Continued*)

For a two dimensional model where each dipole sits on a square lattice where each lattice spacing is a, it is easy to obtain an analytical solution for the nearest neighboring approximation:

$$U^{(0)} = [-3nl + 2n + l]u_0 \tag{5.3}$$

where $u_0 = p^2/a^3$ and $nl = N$. The N dipoles are arranged in n row and l column, where each row of the dipole has the dipole moment pointing in the same direction along the lattice point. The dipole moments of the next row has just the opposite direction. The dipole moments in our model are restricted to point only two ways. If we include the next set of neighboring dipoles which have the strongest interaction, the additional interaction energy is

$$U^{(1)} = \left[\left(-\frac{1}{4} + \frac{\sqrt{2}}{4} \right) nl + \left(\frac{1}{2} - \frac{\sqrt{2}}{4} \right) n - \frac{\sqrt{2}}{4} l + \frac{\sqrt{2}}{4} \right] u_0. \tag{5.4}$$

It is possible to find the configuration with the minimum interaction energy $U = U^{(0)} + U^{(1)}$. The shape is rod-like with the ratio r of length l to width w to be

$$r = \frac{l}{n} = \frac{(5/2)-(\sqrt{2}/4)}{l-(\sqrt{2}/4)} \approx 3.3 \ . \tag{5.5}$$

It is an elongated object as indicated by electron microscope pictures. This is displayed in Fig. 4. The experimental values of the ratio r peaks sharply at the theoretical minimum of 3.3 with a spread from 1 to 14.
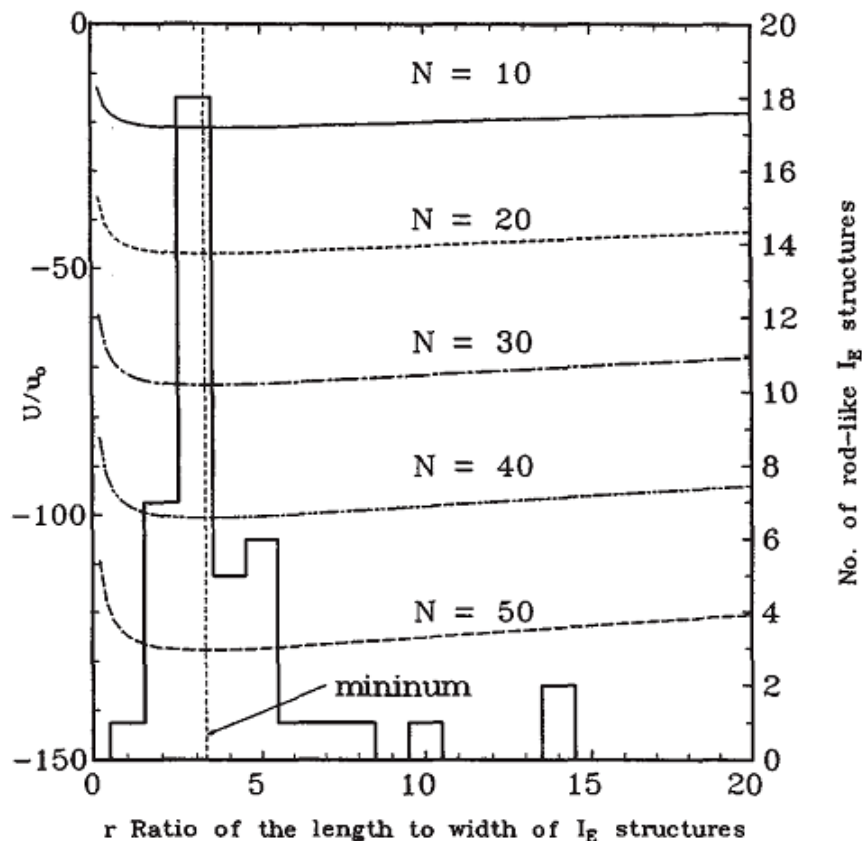

Fig. 4. Dipole–dipole interaction energy of rod-like I_E structure in dimensionless unit U/u_0 versus the ratio r of its length to width. N is the number of dipoles in each rod-like I_E structure. The histogram are numbers of rod-like structures from electron microscope pictures with a given ratio r.

6. Summary

There are considerable experiments in the field of biology, biochemistry and pharmacology indicating that ultra low doses have significant effects on living organisms.[4] Our experiments here show that ultra small amounts of acid, base or salt can induce a stable rigid I_E structures in water itself. These I_E structures have different UV transmission characteristics from pure water. Transmission electron microscope pictures are consistent with the idea that these I_E structures are made up of electric dipoles. Further physical properties of I_E structures will be presented in a separate paper.

Acknowledgment

References

1. N. Fletcher, *The Chemical Physics of Ice* (Cambridge University Press, 1970), Fig. 5.4.
2. We use water produced by Millipore RO Plus system that guarantee purity of water to less than several parts per billion of impurity.
3. Similar I_E structures are also seen using Atomic Force Microscope directly. They have also been studied successfully *in situ* by laser autocorrelation method to be published.
4. In *Ultra Low Doses*, edited by C. Doutremepuich, Taylor & Francis, London, Washington D.C. (1991).