Review Article:

Imperfections in the Aqueous Lattice of Clathrates, as Detected by Electron Trapping

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Abstract. X-ray analysis has been used to elucidate the structure of hydrates, especially of aqueous clathrates, but it has not given information on imperfections occuring in crystals. Other methods, sensitive to the disturbance of structural periodicity, have to be applied to detect and identify the defects. Pulse radiolysis shows identical, intense transient spectra in a group of hydrates which exhibit certain common features. The spectrum ($\lambda_{max} = 620\,\mathrm{nm}$) is tentatively ascribed to the electron trapped in a single water molecule vacancy in the aqueous moiety of the crystal. The pre-existing specific defect is formed during the crystallization process. The optical absorption spectrum is similar to the hydrated electron spectrum in liquid water or aqueous solutions. The nature of the traps is deduced from the known structure of clathrates, in which small anions substitute for one water molecule and may be displaced. Among investigated salt hydrates, amine hydrates and true clathrate hydrates, not all compounds show the ability to trap electrons. The present paper discusses the conditions for the occurrence of water molecule vacancies in the aqueous moiety of the clathrate and the general aspects of the observed phenomenon. A need to investigate imperfections by other methods is also stressed, although such alternatives are not yet available.

Key words. Amine hydrates, aqueous clathrates, hydrates, lattice imperfections, point defects, tetraalkyl ammonium salts, water molecule vacancy.

1. Introduction

The solid crystalline state is always associated with a variety of imperfections. Various methods of crystallization may result in a different set and concentration of crystalline defects, but the preparation of totally imperfection-free crystals is impossible. In fact no crystal can be perfect at finite temperatures. Imperfections appear, even in the case of carefully grown single crystals, because of molecular movements affecting the elements of the lattice during the arrangement into an ordered structure. The pattern of imperfections may be modified later both in the direction of decreasing or increasing the types and quantities of defects.

Although clathrates, semiclathrates and most non-clathrate hydrates are crystalline substances of well known structures, there is no interest as yet in imperfections, in spite of their obvious presence. There are several reasons for this state of affairs: in the case of hydrates in general, imperfections do not manifest themselves easily. One of the reasons for the low interest is the lack of applications, at least in the near future. There is no comparison with the field of semiconductors where the lattice imperfections play a key role. The main technique applied in the determination of lattice parameters, i.e. X-ray structural analysis, is not sensitive to the

defects in the crystal. Other techniques, which are specific to geometrical and energetic imperfections, rather than to the average positions of atoms in the lattice, have not yet been applied. It is the technique of specific interaction of an imperfection with an introduced agent, which is able to give information supplementary to the structure detected by X-ray techniques.

In our studies of the radiation chemistry of nontypical aqueous systems, we have discovered indications of the presence of water molecule vacancies in the aqueous moiety of clathrates [1, 2]. The results and conclusions may be of interest for inclusion compound chemistry.

2. Compounds Showing the Presence of Imperfections

The description of materials used is given in some detail, since it is especially important to specialists in inclusion compounds. Several aqueous clathrates and semiclathrates have been chosen as the object of investigation. The compounds selected had to be rich in water and reasonably transparent when examined as polycrystalline conglomerates.

1. *Tetra-n-butylammonium hydroxide clathrate.* $(C_4H_9)_4NOH \cdot 28-30 \ H_2O$, referred to as TBAOH·29 H_2O. This compound is experimentally most convenient, because of its comparatively high melting temperature of $+28°C$ and its facile preparation in the spectrophotometric cell. It is investigated in the polycrystalline state of high transparency resembling an aqueous solution, or the frozen glasses widely used in radiation chemistry. The starting material was a 40% aqueous solution of tetra-*n*-butylammonium hydroxide, supplied by almost all reagent distribution firms. The first step was the preparation of the solid clathrate containing 28–30 H_2O molecules per single TBAOH molecule, by crystallization under slow cooling to 20°C. The exact content of water, observed sometimes to be different inside the same large crystal, was shown not to be critical for the occurrence of the phenomena described below. Selected crystals of the clathrate were melted into the working vessel, e.g. a 5 or 10 mm optical path length Suprasil cell. If no UV investigations were needed, cheap plastic (polystyrene or polyacrylic) disposable spectrophotometric cells were used. Melted preparations were always nucleated by chosen crystals and cooled slowly. Operations in Suprasil cells are difficult and risky, because removal of the sample may easily lead to the destruction of an expensive vessel. The densities of the molten and solid clathrate are the opposite of those in the water–ice system. The solid clathrate $(d = 1.05)$ expands when melted $(d = 0.987)$.

2. *Tetra-n-butylammonium fluoride clathrate* was chosen as a similar entity to TBAOH·29 H_2O, but of neutral pH in the liquid state. The compound, $(C_4H_9)_4NF \cdot 32 \ H_2O$, referred to as TBAF·32 H_2O, was prepared from the commercial reagent supplied as the trihydrate of poor purity. It had to be separated from an unidentified compound of low solubility. The pH was controlled throughout the preparation at a value of 7. The crystallized clathrate was melted ($+25°C$) as usual into the spectrophotometric cell, nucleated and investigated in a polycrystalline state. TBAF·32 H_2O incorporates substantial amounts of N_2, visible as bubbles during melting. The presence of nitrogen has no influence on the phenomena described.

3. *Tetra-n-butylammonium oxalate clathrate* was chosen as an example of clathrates with large anions and cations. The compound, $[(C_4H_9)_4N]_2C_2O_4 \cdot 38\ H_2O$, TBAOx·38 H_2O for short, belongs to the group of clathrates melting below room temperature ($+17°C$), thus demanding a moderate cryogenic approach. The clathrate was prepared from the already purified TBAOH, by neutralization with oxalic acid.

4. *Diethylamine clathrate*, $(C_2H_5)_2NH \cdot 8\frac{2}{3}\ H_2O$, begins the list of amines which protonate in solution and which were therefore suspected of developing similar imperfections to TBAOH·29 H_2O and TBAF·32 H_2O. The melting point is $-7°C$ and the preparation proceeds from the pure amine by stoichiometric mixing with water and careful crystallization.

5. *tert-Butylamine clathrate*, $(CH_3)_3CNH_2 \cdot 9\frac{3}{4}\ H_2O$, is prepared from the amine as described above, but under an overpressure (150 kPa) of nitrogen. N_2 is incorporated into the structure and for some reason improves the transparency of the sample, without changing the electron trapping chemistry.

6. *Trimethylamine clathrate*, $4(CH_3)_3N \cdot 41\ H_2O$ was prepared from 25% reagent grade aqueous solution. The melting point is $+4°C$.

7. *Piperazine hexahydrate*, $C_4H_{10}N_2 \cdot 6\ H_2O$ is sometimes called a semiclathrate because it differs from a true clathrate. In the piperazine hydrate, hydrogen bonds exist between the aqueous moiety and the guest molecule. For that reason the investigation of this particular compound seemed to be interesting. The reagent was used as supplied and crystallized from the melt to improve the transparency.

Many other clathrates and semiclathrates are not mentioned because of the limitation on the length of the present paper. Some clathrates selected for investigation, such as the tetra-*iso*-amylammonium hydroxide hydrate, did not seem to yield qualitatively new results.

3. The Detection of Imperfections

Radiation chemistry is seldom performed in connection with inclusion compound research. The interest of radiation chemists in the solid state is in general low, since the rigid state (e.g. gels) and glasses are not considered to be true solids. The technique of research in radiation chemistry consists of treating a sample with ionizing radiation, usually gamma rays or accelerated electrons. The first kind of energy is useful only if stable products are observed. More interesting are transient products, but they may be investigated only by a pulse radiolysis method. Electrons accelerated to the energy of several MeV create in the irradiated sample a sufficient concentration of transient products during the microsecond, or even nanosecond pulse. Intermediate, transient products, usually of exotic composition (free radicals, radical ions) may be detected by time-resolved spectroscopy and sometimes by electrical conductivity and other techniques. Kinetic measurements give information about the mechanisms of decay. Modern installations for pulse radiolysis are usually computerized and also the processing of data has benefited enormously from modern techniques. The present research into inclusion compounds would have been much slower without these developments. For instance the poor transparency of some polycrystalline samples is better tolerated, because satisfactory signal-to-noise ratios may be achieved.

The reported results have been obtained on three pulse radiolysis installations, differing in the pulse power and length. First observations of an electron trapped in TBAOH·29 H_2O were achieved in the early eighties on the 13 MeV electron Linac in Warsaw [3], which delivers very high doses of radiation. The bulk of the data has been collected in the Radiation Laboratory, University of Notre Dame, and supplementary measurements were performed at the CFKR in Austin, Texas. Recent work has been carried out in the Institute of Nuclear Chemistry and Technology in Warsaw.

The dominant transient spectrum in the aqueous clathrates listed above, and also in many nonlisted, nonclathrate hydrates, is an absorption band, broader than in liquids, with a maximum at 620 nm. It has been identified as the spectrum of electrons trapped by surrounding water molecules and is similar to the hydrated electron trapped in liquid water and aqueous solutions (maximum between 700 and 720 nm). The hydrated electron is symbolized as e_{aq}^-, and our entity is called $e_{t(aq)}^-$ to show both the similarity with, and difference to, the well established hydrated electron (Figure 1).

The characteristic spectrum of $e_{t(aq)}^-$ is not influenced by the nature of the guest in the clathrate and the presence or absence of hydrogen bonds between the guest and host does not play any role. Not all hydrates show the trapped electron spectrum. There are cases in which there is no spectrum at all, e.g. in the acetone clathrate. One can also note that pure ice does not show the transient absorption of the type mentioned, unless it is properly doped.

The spectra of the trapped electrons are very similar in different aqueous clathrates but marked and characteristic differences occur in the kinetics of decay. Two typical patterns may be observed – one of very short decay (a half-life of a few microseconds) and a longer one, from several hundred microseconds to milliseconds. All decays are first order; Figure 2 shows a typical example.

In some cases both populations of differently trapped electrons occur simultaneously. Figure 3 shows the decay of electrons in TBAOH·29 H_2O, followed at
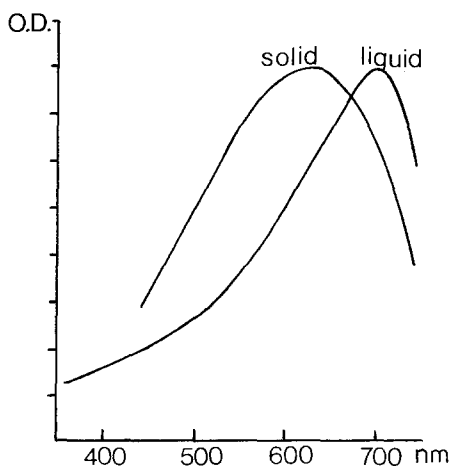

Fig. 1.   Spectrum of $e_{t(aq)}^-$ denoted 'solid' in the clathrate and of e_{aq}^- ('liquid') in the molten sample. Optical densities normalized to the maximum of absorption.
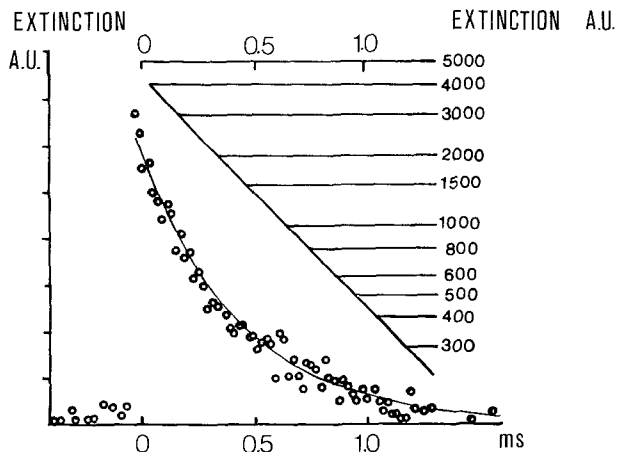
Fig. 2. Typical decay curve of the electron trapped in the clathrate. Optical density (AU) followed at 620 nm. The scale at right is log O.D.
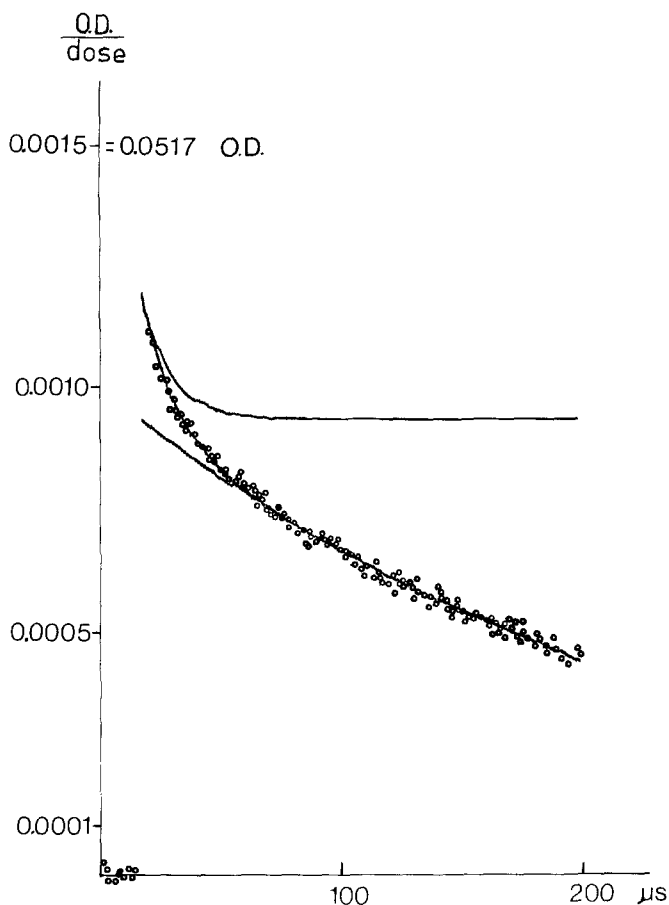

Fig. 3. An example of short lived and long lived trapped electrons present in one sample. The decay is resolved into two first order processes. The half-life time of the fast process is 8.1 μs and of the slow process is 168 μs.

620 nm. The decay is clearly divided into a fast and slow component. Computer-assisted resolution of the recorded curve into two superimposed first order processes gives the rate constants and half-life times. Twenty percent of electrons decay rapidly. There is probably a competition between two kinds of traps for electrons created in the sample. We will not discuss the question of the trap structure and detrapping mechanism here. One can note only that in TBAOx·38 H_2O there is only the short lived variety, a fact that is important for the interpretation of trapping in terms of lattice imperfections. Piperazine hydrate shows only the long lived variety, with the longest lifetime (milliseconds) observed to date.

There are as yet no well founded assumptions as to the identity of short lived electrons, and in the present paper that intermediate will not be discussed, since one must wait for more experimental and/or theoretical clues. Most probably a different type of aqueous trap is involved.

Observations on long lived electrons are sufficiently interesting. First of all, there is a striking similarity between the spectra and kinetics in the case of TBAOH·29 H_2O and TBAF·32 H_2O. It shows that OH^- is not necessary to cause the phenomenon of trapping. The full importance for the interpretation may be seen in the Interpretation section, below.
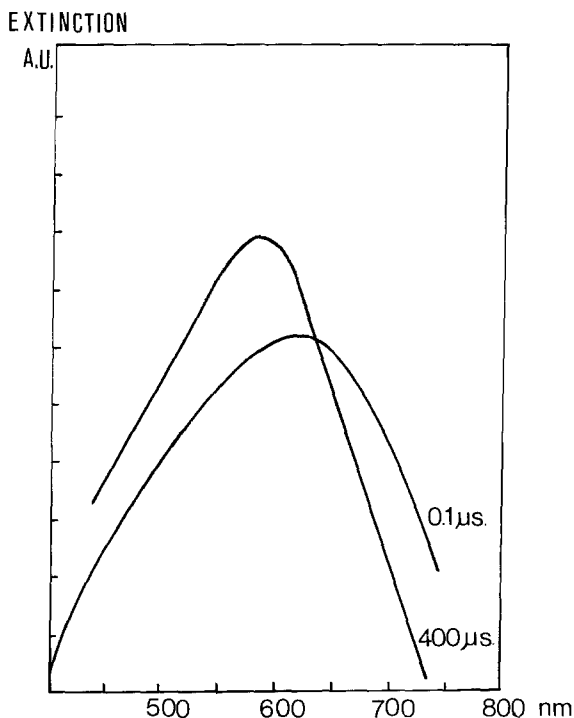

Fig. 4.   Change of absorption spectrum of the trapped electron in TBAOH·29 H_2O at 170 K between 0.1 μs and 400 μs after the generating pulse. The trapped electron decays much slower at that temperature in comparison to room temperature. Before the decay, the change of the electron-trap structure occurs, as shown by the change of spectrum shape, location of maximum and the half-width.

Many experiments have been performed at lower temperatures, down to 100 K. The decay of $e^-_{t(aq)}$ slows down and the activation energy of decay in the first zone, beginning with room temperature, is 0.045 eV for the main, slow component in TBAOH·29 H_2O. Interesting phenomena are observed at 170 K, where the decay is slow and cannot even be noticed on the millisecond scale. During the first 200 μs the entity [electron + trap] rearranges, as we can see from the blue shift of the maximum from 630 to 575 nm (Figure 4). The half-height-width narrows at the same time. There is also a similarity of the observed time of the rearrangement with the relaxation time of water molecules in a similar clathrate at low temperature, as measured dielectrically [5]. Unfortunately, TBAOH·29 H_2O has not yet been investigated for dielectric properties at low temperatures.

4. Interpretation of Experimental Data

A preliminary inspection of results showed that there are clear differences between the types of hydrates. Transient spectra which can be ascribed to the trapped electron by analogy with other aqueous systems, appear to exist only in the salt and amine hydrates where there is a strong guest–host interaction. In pure ice and acetone hydrate, where there are no strong guest–host interactions, electron traps appear to be absent. A more detailed analysis requires a knowledge of the chemistry of the lattice imperfections and of traps interacting specifically with electrons.

Before starting the interpretation of observations in terms of imperfections in hydrates, let us mention the classic case of trapping of electrons generated in the solid state. The so called F-centre (Farbzentrum) is one of the oldest-known radiation induced phenomena, consisting of the trapping of an electron in the preexisting anionic vacancy of the ionic crystal (Figure 5). This textbook example states that the point defect is occupied by the electron which oscillates with a frequency depending on the size of the cell. According to these dimensions, the irradiated material exhibits an optical absorption spectrum. With small vacancies, as in LiCl, the absorption occurs in the UV, but in large vacancies (NaCl, KCl) it appears in the visible region. In very large vacancies (CsBr) the absorption shifts toward the IR. The entity [electron + trap] in alkali halides is usually stable until it is bleached photochemically (resonance wavelength) or thermally.

The assumption that the trapping of electrons in clathrates and other hydrates may be similar to F-centres was abandoned very quickly, because it was inconsistent
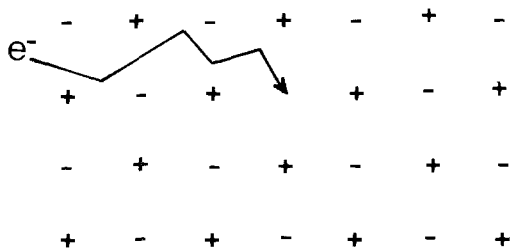

Fig. 5. Simplified structure of an alkali metal halide with an anionic vacancy. The slowed down electron is trapped in the vacancy.

with experimental facts. For instance the spectra were not dependent on the size and chemistry of the guests. Also, in nonclathrate hydrates of low water content, there was very little or no influence of the size of the cation. A close resemblance of observed spectra and kinetics to other known aqueous systems lead to a concept that we are dealing with some sort of trapping of electrons in the aqueous moiety of the clathrate.

When examining the nature of trapping in clathrates one has to consider the possibility of the formation of traps by radiation. In the case of a low LET (linear energy transfer) radiation (gamma and electrons) the formation of traps proceeds with a low yield. Even with light atoms in the sample, elastic collisions leading to a displacement in the lattice do not proceed efficiently in comparison to the action of heavy ionizing particles. The textbook example says that gamma or beta (electron) radiations need *ca.* 100 keV radiation energy to create one defect (assuming 25 eV for creation of a permanent displacement) whereas energy in the 30–90 eV range of protons, alpha particles or neutrons is sufficient to produce the same effect.

Assuming the standard dose in the majority of experiments to be 3 Gy (300 rads) or 1.87×10^{19} eV/g per pulse, the energy needed to create elastically a displacement indicated above, and considering the composition of the clathrate, we obtain *ca* 1.3×10^{14} defects formed per gram per pulse in the aqueous moiety. The efficient participation of accelerated electrons in trap formation may be rejected. Therefore the key role must be attributed to preexisting traps.

The origin of preexisting traps in clathrates may be deduced from the analysis of X-ray structural data that was carefully performed in the sixties. There is no need to describe the structure of clathrates which are available in excellent reviews and monographs [6, 7]. The key information is a finding of the Jeffrey school, which was not subsequently elaborated. They concluded, on the basis of structural investigations, that small anions (OH^-, F^-) in the tetraalkylammonium clathrates do not occupy voids, because of their small size, but substitute for one water molecule in the aqueous lattice (Figure 6). If so, during the crystallization the anion may be missing, leaving a water vacancy. Even if only 1% of the OH^- or F^- sites are vacant, it gives a concentration of 15 mM for electron traps, i.e. a concentration more than sufficient to trap all electrons produced even in the largest pulses of radiation.

The modest assumption that 1% of OH^- (or F^-) are missing yields 5×10^{18} vacancies of H_2O per gram. This is a much higher value than the 1.3×10^{14} defects created (at most) by radiation. The latter, even if of similar energy in comparison to preexisting defects, cannot efficiently compete for electrons. Created traps might have been accumulated during sequential pulses, but even after 1000 shots (3 kGy) they will be at a lower concentration than the preexisting vacancies. Anyway, there are no changes in spectra and kinetics after massive doses, and also the creation of radiation induced traps in vacancy-free clathrates (e.g. the acetone clathrate) has not been successful as yet.

X-ray investigation does not give information about the possible sites of vacancies in the case of amine clathrates. We can accept a similar mechanism, because molten clathrates of all the amines investigated are strongly alkaline, due to protonation. Our methylamine melt has a pH of 12.8, *tert*-butylamine 12.6, trimethylamine 12.0 and piperazine 11.9. It means that these liquids contain, at the
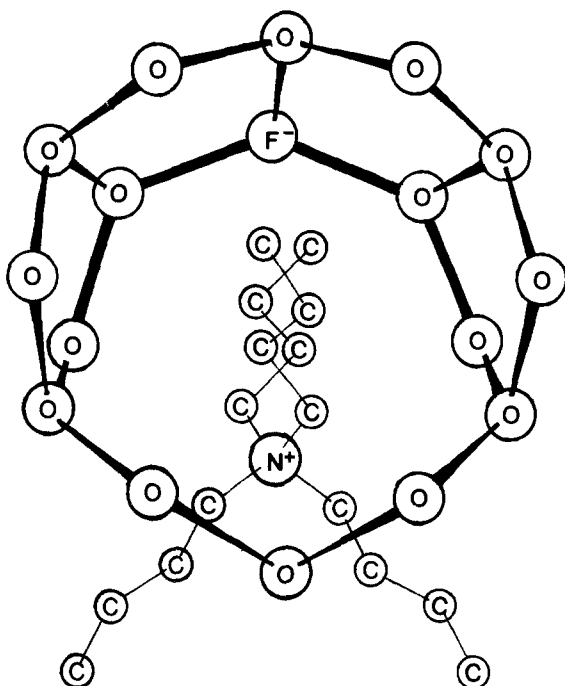
Fig. 6. Projection of a part of the TBAOH (or TBAF) clathrate lattice. Only essential elements are shown. All hydrogens at carbons and oxygens are omitted for clarity. The anion (F^- or OH^-) exchanges one molecule of water in the aqueous moiety of the clathrate. Simplified from the paper by McMullan, Bonamico and Jeffrey [8].

time of crystallization, concentrations of OH^- of the order of tens of mM. Hydroxyl ions are present during the process of crystallization and can substitute water molecules in the lattice exactly like OH^- or F^- in the discussed cases. Consequently there is a possibility of point defect formation, leaving H_2O vacancies among the water molecules. The structure of the trap must obviously be very similar. There are chances for observation of saturation phenomena in amines because of the lower concentrations of traps, but they have not yet been explored. One pulse of radiation saturates about 0.1% of the traps available in amines, if our estimate is correct. Therefore the competition for electrons may be lower and that has already been observed.

Concerning the classification of the defects in hydrates, there is no proposal of notation, because these defects have not been described yet. The assumed defect is a neutral vacancy, in contrast to an anionic vacancy in halides, where it is charged with respect to the lattice. The vacancies in our case may belong to the V_k; V_x type in the commonly used Kroger–Vink notation.

The trapping of electrons in vacancies may be located in the group of so called sensitive properties [9] for detection of imperfections. Neither type of effect and imperfection invoked by Kroger (Table 8.1 in [9]) matches the phenomena described in the present paper. The best place in the systematic approach would be

under point 4 ('Trapping effects') with the special description of 'Optical spectra and decay curves of trapped electrons'. The type of imperfection involved would be 'Vacancies of energetics and geometry specific to trap electrons'.

It is not easy to estimate the lower detection limit of the observed vacancies (in ml^{-3}). The trap, a vacancy of one water molecule, is not the only partner of reaction with the electron. The latter has many options for reaction depending on the system. Therefore the trap enters into competition with other partners of different reaction cross-sections and of different concentrations. If the traps occur in low concentration, they cannot gather all the available electrons but only a part of them. This is already visible in our systems. Vacancies in protonated amine clathrates occur in lower concentrations than in TBAOH·29 H_2O, and they cannot trap all electrons. The availability of traps is not sufficient to eliminate other partners, e.g. the positive counterpart of the detached electron and hydrocarbon radicals in the guest, to name only two possibilities of electron reactions.

One has to stress that the above analysis concentrates only on imperfections interacting selectively, by proper geometry and energetics, with electrons. It does not mean that pure ice and acetone clathrate are free of imperfections. They are only comparatively free of specific single vacancies of water molecules. The above-mentioned solids probably contain a variety of other imperfections, for which detection systems like the trapping of electrons has not been found yet. All solids show the presence of different sets of imperfections. Only liquids and glasses have an almost continuous spectrum of imperfections of different size, shape etc.

5. Conclusions

At least one type of imperfection in aqueous clathrate and semiclathrate crystals is proposed to be a single water molecule vacancy in the aqueous moiety of the lattice. That assumption is based on the most plausible explanation of the trapping of electrons in hydrates, as detected by the pulse radiolysis method.

As the existence of lattice imperfections in hydrates has been presented for the first time, it would be advantageous to support or modify the view presented, by the application of other methods of solid state chemistry, or physics sensitive to defects in crystals. In the case of hydrates an alternative approach does not seem to be available yet.

Acknowledgement

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