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Ionic clathrates from aqueous solutions detected with laser induced liquid beam ionization/desorption mass spectrometry

Frank Sobott, Andreas Wattenberg, Hans-Dieter Barth, Bernhard Brutschy*

Institut für Physikalische und Theoretische Chemie, J. W. Goethe-Universität, Marie-Curie-Str. 11, 60439 Frankfurt am Main, Germany

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Abstract

Clathratelike structures of the alkali metal ions $M^+ = Li^+$, Na^+, K^+ Cs^+, and ammonium with water molecules have been investigated with laser induced liquid beam ionization/desorption (LILBID) mass spectrometry. The LILBID process implies the desorption of ions from a thin jet of supercooled water in high vacuum by means of an IR laser pulse. Magic numbered water clusters are observed in the cation mass spectra of K^+ and Cs^+ halides, but not for Li^+ and Na^+. Predominant cluster sizes for $K^+ (H_2O)_n$ are $n = 16, 20, 25, 27$, and for $Cs^+(H_2O)_n$, $n = 18, 20, 22, 24, 27, 29$, with the highest signal intensity for $n = 20$. Water clusters of this size correspond to deformed dodecahedral cage structures (clathrates) with a cation in the cavity, which are known to exist in the gas phase and in the solid state. The possible occurrence of clathratelike clusters in the liquid phase is discussed in the context of the physical chemistry of electrolyte solutions and the LILBID experiment. (Int J Mass Spectrom 185/186/187 (1999) 271–279) © 1999 Elsevier Science B.V.

Keywords: Laser desorption; Mass spectrometry; Clathrates; Solvation; Alkali metal ions

1. Introduction

In mass spectra of polymeric compounds or complexes, the appearance of prominent peaks in an otherwise continuous distribution of signals may indicate the existence of species with an enhanced stability, also called “magic number clusters”. Probably the most famous example for magic number clustering is the discovery of fullerenes by Curl, Smalley, and Kroto in a mass spectrum of vaporized carbon condensed in an atmosphere of inert gas [1]. Numerous experiments have been reported which give evidence that magic numbers exist as well for solvent clusters of metal cations. The best examined of these are presumably the water clusters $M^+(H_2O)_{20}$, with $M^+ = H^+$, H_3O^+, $NH_4{}^+$ or an alkali metal ion of sufficient size. The solvent molecules have been found to form a regular arrangement with a cagelike *clathrate* structure [2]. It is well known that clathrates appear in all kinds of natural environments, from deep-sea sediments [3] to nucleation processes in the atmosphere [4]. Upon decomposition, they can cause explosions in high-pressure gas pipelines [3]. It has even been suggested that anesthesia might be attributed to the formation of clathratelike hydrate crystals in the brain [5]. For a summary of clathrate structures, see ref. [6]. The

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* Corresponding author. E-mail: brutschy@chemie.uni-frankfurt.de

Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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study of clathratelike water structures illustrates the principles of hydrogen bonding and solvation [7]. The incorporation of one or more guest molecules by a host structure, which is formed by a framework of solvent molecules, is an important principle in nature. As an effective encagement requires the guest to fit in and fill out the cavity, it represents a prime example for supramolecular recognition by a self-ordered structure.

Various computational methods have been employed to rationalize magic number water clusters. For the $(H_3O)^+(H_2O)_{20}$ clathrate, a pentagonal dodecahedral cage was suggested as the equilibrium structure using the PM3 quantum-mechanical/semiempirical method [8,9]; however, several different structures with almost equal stability have been discussed for $Na^+(H_2O)_{20}$ on the basis of molecular dynamics calculations [10]. While thermochemical considerations indicate that entropic rather than energetic effects give rise to the observed magic numbers, there has been experimental evidence for an enthalpic origin as well (see discussion in Ref. [11]). Monte Carlo simulations of protonated water clusters by Svanberg and Pettersson allow to estimate the melting temperature of $(H_3O)^+(H_2O)_{20}$, which they found to be between 150 and 170 K [12]. According to their data, the Lindemann index (which is a measure for bond length fluctuations) and the average radius of gyration show a distinct increase in the phase transition region, which means that the rigid clathrate framework is destroyed and the water molecules become mobile. Smith and Dang applied molecular dynamics to $Cs^+(H_2O)_n$ clusters with $n = 19$–22 and found a maximum in the incremental binding energy for $n = 20$ only if the mean kinetic temperature was lower than 160 K [11]. It seems reasonable to suppose that clathratelike ordered structures exist only in the solidlike regime, i.e. in the frozen state, and magic-number behaviour in the condensed phase should be restricted to cluster temperatures below the melting point. To sum this up, we want to quote van der Waals' and Platteeuw's definition of clathrates as "solid solutions of a component in the (metastable) host lattice" [13].

Experimental evidence for the occurrence of ionic clathrates is mostly due to mass spectrometry. A variety of different ionization and desorption methods has been applied to the examination of solvent clusters. Castleman et al. used a fast-flow reactor where clusters produced by expanding gas through a nozzle are thermalized by a large number of collisions with carrier gas [14–17]. The temperature of the ion source had to be lower than 130 K for water clusters, and alkali metal ion clathrates could only be observed below 170 K. This corresponds well to the results of the above mentioned theoretical studies on the melting point of magic number clusters. For a summary of the work by Castleman et al., see Ref. [18]. Kosevich et al. did experiments with fast-atom bombardment on low-temperature ice surfaces [19]. Only the monohydrate of Na^+ appeared in the mass spectra when the sodium salt was on the ice surface; largely hydrated Na^+ clusters showed up solely when the sodium salt had been deposited beneath a thin layer of ice or in small crystallites. In the opinion of the authors, ions are formed in the dense plume around the impact site of the bombarding particle in the first case, whereas in the latter the sublimation of material over the whole surface of the sample allows large clusters with less internal energy to form. Recently, electrospray ionization has been applied to the examination of water clathrates as well [20,21]. Clusters of hydronium and ammonium ions with more than 200 water molecules have been detected in pure water and ammonia–water mixtures. The gradual dissociation of large water clusters in a ion cyclotron resonance cell induced by black body radiation reveals different mechanisms for the decomposition and stabilization of metal ion hydrates in the gas phase [22].

We report the application of a new mass spectrometric technique that is called laser induced liquid beam ionization/desorption (LILBID), to the examination of alkali metal clathrates in aqueous solutions. The detection of cesium clathrates with LILBID has already been reported in a previous publication [23]. Now mass spectra have been recorded with different alkali metal ions and ammonium at different solution temperatures and desorption laser energies. LILBID, which has been developed in our group, has proven to be a soft desorption method which can be used to investigate ions in the condensed phase, e.g. ion-solvent interactions, under the appropriate experimental conditions. The published work gives an impression of the LILBID process and its implications to the origin of ions. The method has been applied up to now to the following topics: the cation selectivity of natural and synthetic ionophores [24], metal ion binding by a small peptide [25], noncovalent interactions between biomolecules [26], and to condensation reactions of group IV A alkoxides in alcoholic solutions [27].

2. Experimental

The experimental setup of the LILBID apparatus has been described in detail elsewhere [23]. In brief, alkali halides (LiCl: *Fluka*, >99%, NaI: *Fluka*, 99.5%, KCl: *Fluka*, >99%, NH_4Cl: *Merck*, 99.8%, CsCl: *Janssen*, 99.999%) are solved in pure, deionized water at a concentration of 10^{-4} mol/L each. The analyte solutions are then pumped through a PEEK capillary with an HPLC pump (Merck–Hitachi L-6000 A) at a constant backing pressure of 20–50 bar (flow rate 0.1–1 ml/min). Through a 10 μm wide nozzle, a thin, laminar beam of analyte solution is injected into the recipient (Fig. 1). There a vacuum in the range of 10^{-6} mbar can be maintained by freezing out the liquid on a cold trap. The initial temperature of the liquid can be adjusted with a cryostat between -10 and $+60$ °C (at -10 °C, a liquid jet can still be generated with a backing pressure of 50 bar). Additional evaporative cooling in the vacuum region rapidly lowers the temperature by tens of degrees, though. Water may thus be supercooled considerably below its freezing point; surface temperatures as low as -63 °C have been measured in the liquid phase [28]. The liquid jet remains intact up to a critical length of a few centimeters, where it decays into droplets due to Rayleigh instabilities.

At a distance of several millimeters from the nozzle, the liquid beam is irradiated with a pulsed IR laser (10^7–10^8 W/cm^2). The laser wavelength is chosen according to a vibrational absorption band of the solvent, e.g. the O–H stretching vibration of water molecules at 3400 cm^{-1}. The energy transferred to the probe causes a rapid transition into the supercritical state of the liquid with a subsequent explosive expansion of the beam. The laser system consists of a home-build optical parametric oscillator/amplifier (OPO/OPA) with a $LiNbO_3$ crystal which can be tuned in the range of 2700–4000 cm^{-1} (2.5–3.7 μm) and is pumped by a Q-switched Nd:YAG laser (Powerlite 8010, Continuum, Santa Clara, CA) with a pulse length of 7 ns [25]. An energy of 10–30 mJ per pulse is typically required for the desorption of ions from the liquid. For mass analysis, we use a reflectron-time of flight mass spectrometer with an orthogonal extraction geometry and time-lag focusing (delayed extraction). In front of the detector, an electrostatic potential can be applied to reject fragments of metastable ions which might be produced in the flight tube. After postacceleration with 20 kV, ions are detected on an ion/electron converter (Even-cup) coupled with a scintillator and photomultiplier. Spectra are stored with a storage oscilloscope (Le Croy 9410) and read out with a PC.

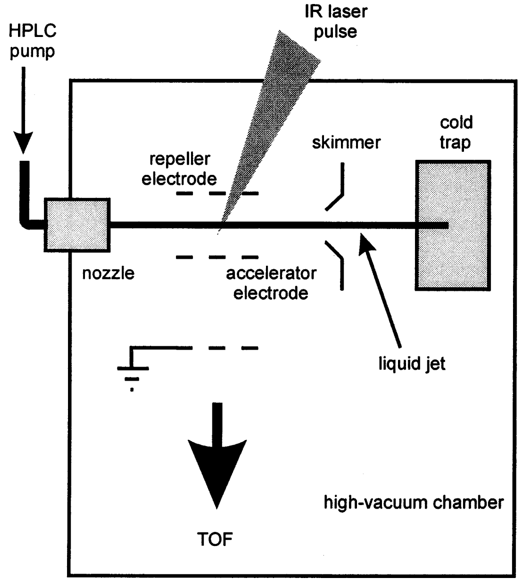

Fig. 1. Schematic setup of the recipient of the LILBID apparatus.

3. Results

Fig. 2 (A)–(E) shows the LILBID cation spectra of 10^{-4} molar solutions of LiCl, NaI, KCl, NH_4Cl, and

CsCl in water at an initial liquid temperature of −10 °C. We tried several halides with various counter ions, but did not find a significant difference in the cation spectra. The fact that signals of the unsolvated Li^+ and Na^+ ion do not appear in the spectra under these conditions can be attributed to the high charge density of these ions, which prevents their desorption and desolvation [Fig. 2 (A) and (B)]. For all alkali metal ions and ammonium, clusters with up to 50 water molecules have been recorded in our experiment. Close to the solvated ion signals, a cluster series with small intensity starts in all spectra at $m/z = 55$ and disappears around $m/z = 300$. This series corresponds to protonated water (hydronium) clusters which are usually found in the cation spectra, even without the addition of acids. The formation of protonated species in solution at neutral pH, where protons are present due to autodissociation of the solvent, has proven to be a key ionization process for LILBID.

The lithium and (to a certain degree) sodium ion give rise to a continuous peak series for $M^+ (H_2O)_n$ with a maximum in the size distribution for $n = 4$, i.e. no magic numbers are observed [Fig. 2 (A) and (B)]. In the potassium spectrum, the signal with the highest intensity is shifted to $K^+(H_2O)_3$ ($n = 3$), and distinctive maxima at $n = 16$, 20, 25, and 27 appear in the cluster distribution [Fig. 2 (C)]. For ammonium, which is roughly of the same size as the potassium ion, the magic number $n = 20$ is found as well. The intensity shift at $n = 10$ is due to underlying water clusters which cannot be resolved from ammonium clusters above $m/z = 200$ [Fig. 2 (D)]. For cesium as the largest ion in this series, several magic numbers are found in this experiment: $n = 18$, 20, 22, 24, and, with less intensity, $n = 27$ and 29 [Figs. 2 (E) and 3]. These cluster sizes refer to clathrate structures which have been suggested by Selinger and Castleman on the basis of gasphase experiments at a temperature of −117 °C (156 K) [16]. The dodeca-

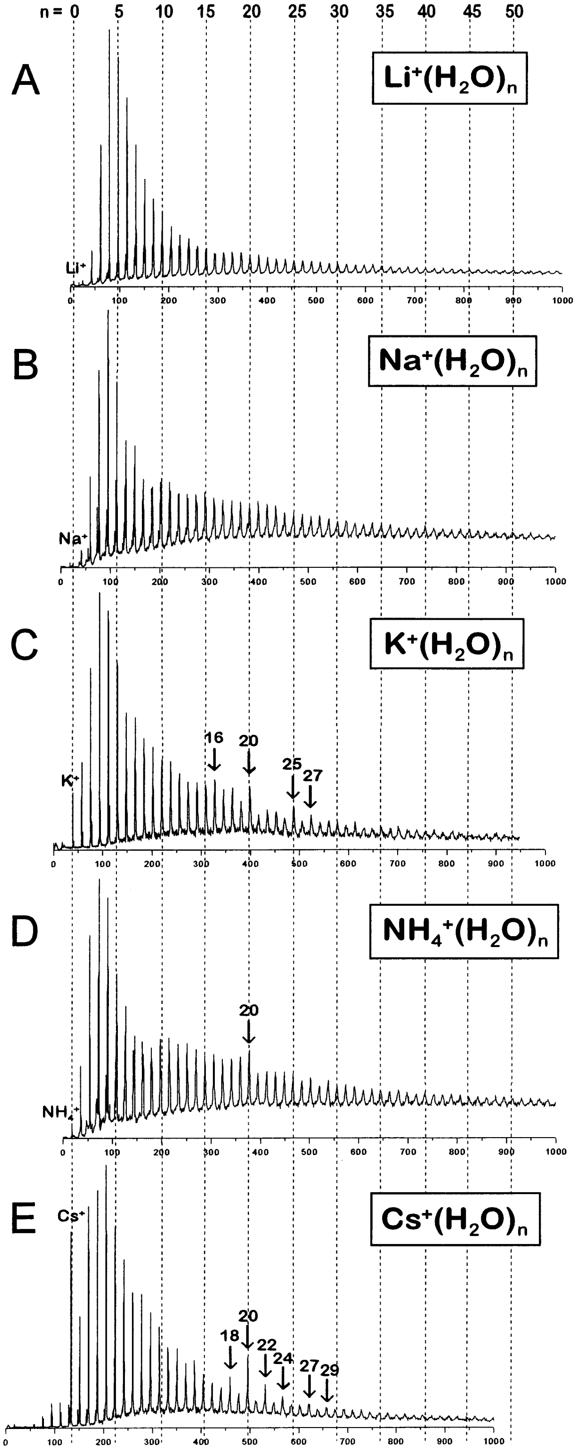

Fig. 2. LILBID cation spectra of solutions of (A) LiCl, (B) NaI, (C) KCl, (D) NH_4Cl, and (E) CsCl, each at 10^{-4} mol/L in water; initial liquid temperature: −10 °C. Some magic number clusters which correspond to clathrate structures have been indicated.

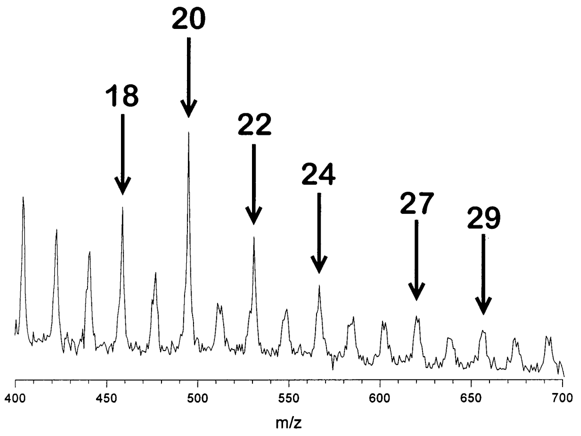

Fig. 3. Expanded section of Fig. 2 (E). The number *n* of attached water molecules is indicated.

hedral structure which they suggested for $Cs^+(H_2O)_{20}$ is depicted in Fig. 4. The other magic numbers correspond to deformed dodecahedrons; in the case of $n = 27$ and 29, one of the water molecules is encaged together with the cesium ion. The rather large cesium ion (radius: 167 pm) should best stabilize the cavity formed by the network of water molecules. Accordingly, Steel et al. have found with their fast-flow reactor that the K^+ and Cs^+ -clathrates with $n = 20$ are prominent at −110 °C (163 K), and a slight preference for this cluster size was seen for Li^+ as well [17]. They showed that these structures are thermodynamically stable in the gas phase, as they survive lots of collisions in the flow reactor. For the potassium ion, additional magic numbers were $n = 16$, 25, 27, and 29, and for cesium, $n = 18$, 22, 24, 27, and 29. These findings are in excellent agreement with our results, although they were obtained under largely different conditions of ion formation and desorption.

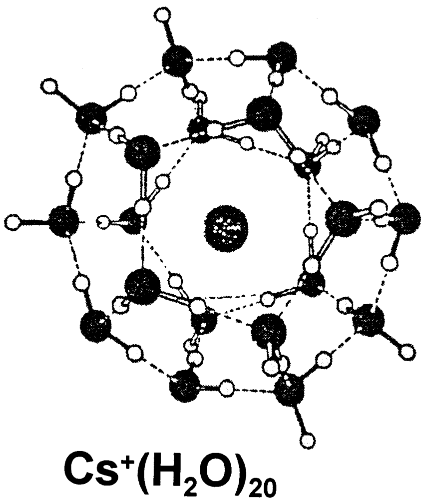

Fig. 4. Proposed dodecahedral structure for $Cs^+(H_2O)_{20}$ [16].

We varied the initial temperature of the liquid between −10 °C (263 K) and +60 °C (213 K) for a 10^{-4} mol/L CsCl solution (not shown). Besides a tendency to form smaller clusters at higher temperatures, we did not find a significant influence on the relative intensity of the $Cs^+(H_2O)_{20}$ peak, which was still visible at +60 °C. It has to be considered though that after expansion in the nozzle, the solution is efficiently cooled in the vacuum by tens of degrees, so that the initial temperature does not play a major role. To a large degree, the clathrate signals are also independent of the position of the laser focus along the liquid beam. Since an increasing distance from the nozzle in the laminar flow regime of the jet corresponds to a decrease in the liquid temperature, this can be regarded as further evidence that clathrate signals are largely independent of the temperature under these conditions.

The amount of energy transferred to the probe by the desorption laser pulse is expected to have a profound influence on the process of ion desorption and desolvation. To examine this influence, we varied the laser energy per pulse between ~13 mJ [Fig. 5 (A)] and 23 mJ [Fig. 5 (B)]. A remarkable effect was found on the overall signal intensity, which increases for higher energies, as well as on the relative amount of clustering, which is higher for low energies. However, the relative intensity of the $Cs^+(H_2O)_{20}$ peak remains unchanged, only the $Cs^+(H_2O)_{22}$ signal is depleted at high desorption energies (see insets in Fig. 5). It can be concluded that with an increasing amount of energy deposited in the solution, more ions are set free, but due to an excess of thermal energy partial desolvation of the clusters sets in. The higher the thermodynamic stability of the clusters, the less they are depleted in the spectra by gas-phase dissociation

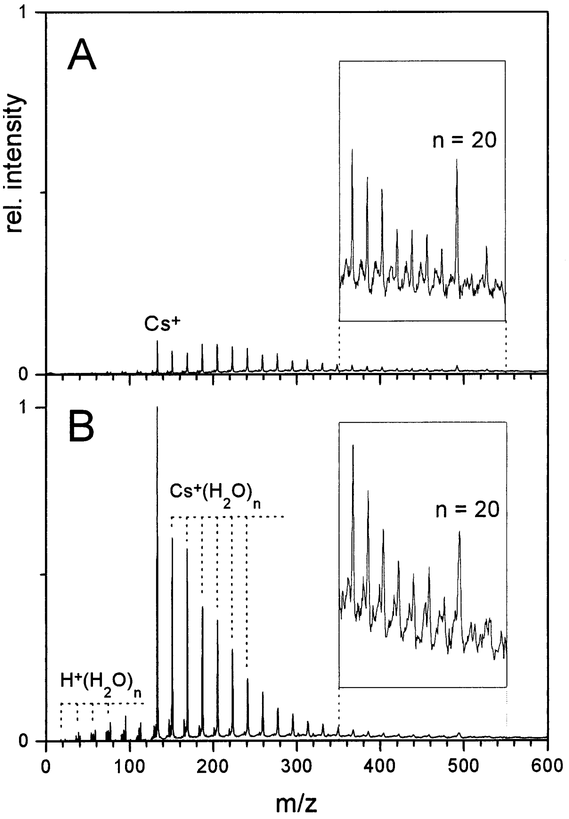

Fig. 5. Influence of laser energy on the detection of cesium solvate clusters: (A) ~13 mJ per pulse, (B) ~23 mJ per pulse at a wavenumber of 3400 cm^{-1}. Inset: expanded spectrum in the range of $m/z = 350$–550.

due to an increased amount of internal energy. Thus by varying the laser power, a simple separation between clusters of different stability becomes possible.

4. Discussion

An interesting aspect pertains to the question whether these magic number clusters are solely produced by thermally induced desolvation of the ions in the gas phase, or whether they are preformed species in bulk phase water close to or below the freezing point. Clathrate structures may play an important role in the solvation of large ions and in the process of freezing, and they might be responsible for the density anomaly of water around the freezing point [6]. While most of the experimental evidence for ion–solvent clathrates has been given up to now in gas-phase experiments, it is well known that neutral methane clathrates exist in the condensed phase at low temperatures and under high pressure [3] (see also the review on “clathrate solutions” in [13]). To our knowledge, it is not known whether this applies to metal ion clathrates as well. The origin of magic number clusters is an important aspect in this context, as it can give a clue to the process of ion formation and desorption for the various mass spectrometric techniques.

Echt et al. studied the formation of the magic-number water clusters $H^+(H_2O)_{21}$ and $H^+(H_2O)_{28}$ in a water vapor jet ionized by a 40 eV electron beam [29]. They found that a drop in the intensity of the cluster signals after the 21-mer and 28-mer appeared only if the rejection potential in front of the detector is raised to 99.4% of the average acceleration potential in the ion source. At this level of the high-pass energy filter, all metastable cluster fragments produced by the evaporation of neutral water molecules from the precursor (which thus lost part of its kinetic energy) are rejected, whereas stable cluster ions, e.g. with clathratelike structure, pass the rejection field unchanged and dominate the mass spectra. However, with an energy barrier lower than 74% of the primary kinetic energy of the clusters, no intensity anomalities are detected and a smooth, exponentially decreasing series of $H^+(H_2O)_n$ signals is obtained. The authors of the study could thus prove, that when the ionization/desorption process takes place in the gas phase, magic number clusters evolve by depletion of the 22-, 23-, and 29-mer in a time window of 4–40 μs after the ionization, while they are in the flight tube of the mass spectrometer. We believe that this process for the formation of magic number clusters in the gas phase does not apply to LILBID, where ions are desorbed directly from the probe solution. When the rejecting field is varied over a broad range from 0% up to 95% of the acceleration field in our experiment, clathrate signals do not change significantly, which means that the corresponding clusters are produced during the desorption process or present in the solution from the beginning. This raises the question whether clathratelike structures of water molecules around an alkali metal ion may exist in the solution, and if so, under which conditions. We want to discuss this point now further in the context of the physical chemistry of solutions of strong electrolytes.

A lot of research has been dedicated in the last 50 years to the understanding of solvation, a phenomenon which—despite its importance for all aspects of chemistry and biochemistry—is still not very well understood. The most elemental concept for the characterization of the state of an ionic species in aqueous solution is its hydration number, i.e. the number of "coordinated" water molecules. However, the hydration numbers found with different experimental methods vary considerably, e.g. for Na^+ values from 1 up to 71 have been reported [30]. The number of water molecules bound to an ion can be estimated, for example, by measuring transport numbers with the Hittorf method, by spectroscopic methods like nuclear magnetic resonance (NMR), or by observing the change in the dielectric constant or entropy upon solvation of the ions (for a review of the methods, see Ref. [31]). Transport numbers are a measure for the ion mobility, which in turn gives an indication of the size of the solvate shell. It has been found with this method that the solvate shell contains on average 5.4 water molecules for K^+, 8.4 for Na^+ and 14 for Li^+ [32]. However, values derived from transport processes refer to the size and nature of *kinetic* entities moving through the liquid under the influence of an electric field, in contrast to the "equilibrium" state of an undisturbed ion contributing to the bulk properties of the solution, which should be obtainable by thermodynamic considerations [33]. Since the structure of water is considerably modified, the dielectric constant is decreased by 13%–18% in 1 mol/L solutions of alkali metal halides compared to pure water [34]. This dielectric decrement is due to the prevention of the rotation of water molecules in the surroundings of the solvate. An average coordination number of 4–6 water molecules has been calculated for lithium, sodium, potassium, and ammonium chloride with this method. The discrepancy between the hydration numbers obtained by various experimental methods is not very surprising, taking into account that they only represent an *equivalent* for the presumably far greater number of water molecules whose properties under investigation are influenced by the presence of the ion. While a few molecules may be bound firmly to the solvate and moving through the solution together with it ("primary" or "chemical" hydration according to Bockris [31]), the farther-reaching polarization effect will influence additional water molecules ("secondary" or "physical" hydration). The various methods for the determination of coordination numbers give a differently weighted average of both types of hydration.

Frank and Wen have suggested a more detailed model for solvation [35]. According to them, an ion is surrounded by three regions that can be distinguished from each other: The innermost sphere, an "iceberg" of closely bound water molecules, is followed by a region, the size of which may vary, where the solvent is disordered as a result of the opposing forces of the ion and the surrounding water molecules, whereas in the third region the water molecules are essentially unperturbed. The influence which an ion exerts on the structure of the surrounding solvent can be inferred from the entropy change of the solution. The experimentally observed entropy loss upon solvation of hypothetical gaseous ions is greatest for Li^+ and Na^+, but considerably smaller for K^+ and Cs^+; it becomes smaller with an increase in solution temperature [36,37]. While the entropy of the water decreases in the inner sphere around the ion, there is a positive contribution to the entropy change for all alkali metal ions except Li^+ connected with the disordering of solvent molecules in the above mentioned intermediate zone. Calculations have shown that this positive entropy term, also called "structure-breaking entropy," is larger for Cs^+ and K^+ than for Na^+ and Li^+, which in part accounts for the overall smaller entropy change in the case of the two larger ions [34].

Samoilov investigated this disordering effect further by considering the exchange frequency of water molecules close to an ion, which he deduced from experimental data on the self-diffusion of water [30]. If the activation energy for the exchange of water molecules close to the ion is higher than in the undisturbed solvent, they are less mobile than the other water molecules. In the opposite case, when it is lower, the water molecules become more mobile than in pure water. In the first case, the ion is said to be "positively" hydrated, in the latter the term "negative" hydration was used. It is interesting to note that Li^+ and Na^+ ions have been found to be positively hydrated, whereas K^+ and Cs^+ are negatively hydrated. The net effect of the large alkali metal ions in this picture would be to disturb the water structure instead of being strongly solvated. Accordingly, Nightingale has divided ionic hydration into four classes, two of which correspond to Samoilov's classification [33]. Of the alkali metal ions, Li^+ and Na^+ are counted among the "structure-ordering ions," while $NH_4{}^+$, K^+, and Cs^+ are denoted "structure-disordering." These terms are corroborated by the observation that the viscosity of aqueous solutions containing ions of the latter group decreases with increasing concentration [33]. A decisive criterion for the structure-ordering effect of an ion seems to be its charge density at the surface, as can easily be seen for the spherical alkali metal ions. Small ions are supposed to cause strong ion–dipole interactions which let the water structure around them collapse in favor of a tight solvate shell [38], whereas large ions "sit" in cavities of the framework formed by the water molecules. With decreasing temperature of the solvent, these cavities will presumably become more and more rigid ("frozen") and might eventually lead into clathratelike structures. These cages would then be stabilized by ions of sufficient size, for example potassium or cesium.

5. Conclusions

Clathratelike cage structures of potassium, ammonium and cesium hydrates have been detected with LILBID mass spectrometry from supercooled solutions. The most prominent magic number cluster is found for $n = 20$. From calculations it is known that this corresponds to a thermodynamically stable, icosahedral cage of water molecules around the cation. Additional magic numbers for K^+ and Cs^+ are in accordance with findings of Steel et al., who used a flow reactor to study clathrate formation [17]. The fact that no magic numbers are observed for the smaller alkali metal ions may be explained by their smaller size and higher charge density, which should destabilize a similar clathrate framework of water molecules. No significant influence of the temperature of the liquid on the occurrence of magic number clusters could be found. However, the amount of IR laser energy changes the relative degree of declustering in the spectra, with the most stable clusters like $Cs^+(H_2O)_{20}$ being the least affected by an increase in laser power.

According to Samoilov and Nightingale, at least two classes of ionic hydration can be distinguished: Positively hydrated or structure-ordering ions like H^+, Li^+, and Na^+, and negatively hydrated or structure-disordering ions like $NH_4{}^+$, K^+, and Cs^+ [30,33]. These terms refer to the effect which the ion exerts on the mobility of the water molecules around itself and which is governed by the ion's charge surface density. As magic number clusters have only been detected for the second class of ions in the LILBID experiment, the absence of a tightly bound solvent shell around the ion seems to be a prerequisite for the formation of clathrates. Although it has been found in the past that LILBID allows the detection of preformed ions from the liquid, it has to be left open however whether these clathratelike structures already exist in cold water, or whether they are formed upon the process of desorption. We hope that future investigations can further elucidate this question.

Acknowledgements

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