Infrared Absorption of Concentrated Aqueous $NaClO_4$ Solutions to High Pressures and Temperatures

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The infrared absorption of the O-D stretching fundamental of HDO in concentrated aqueous $(HDO/H_2O)NaClO_4$ solutions up to 20 mole% salt has been measured. The data for the wavenumber of maximum absorption, $\bar{\nu}(\max)$, and for the integrated molar absorptivity B up to pressures and temperatures of 2800 bar and 250 °C, respectively, demonstrate the importance of non-hydrogen-bonded interactions in aqueous perchlorate solutions. A non-continuous distribution of the states of water molecules is clearly evident from the experimental spectra. A band separation using three Gaussian components proves the close similarity between the high-pressure high-temperature vibrational O-D infrared spectra of aqueous perchlorate solutions and the O-D Raman spectra of water and aqueous solutions.

Results of the band separation together with literature Raman data provide some evidence that a transition from "water-like" to "melt-like" behaviour occurs in a fairly narrow concentration region between 10 and 15 mole% salt.

Introduction

Studies of concentrated aqueous electrolyte solutions are interesting for several reasons: There is an obvious need for a general description of ionic fluids. Numerous experimental investigations and theoretical treatments of the limiting situations, fused salts [1] and dilute aqueous salt solutions [2], are available. Quantitative experimental and theoretical work on concentrated aqueous solutions, however, is scarce [3]. Much more data are needed, and measurements at elevated temperatures and pressures are particularly desirable. An improved understanding of high-pressure high-temperature solutions is also important in geochemistry and for certain parts of power plant operation.

Electrolytic conductance data on concentrated aqueous solutions up to about 600 °C and to high pressures have been published by several groups (e.g. [4, 5]). A useful source of information about the structure in aqueous solutions is, among others, the infrared absorption and Raman scattering of the hydrogen-oxygen stretching modes of the water molecules [6—9]. It has become the established practice to use HDO in H_2O (or in D_2O) as the solvent rather than pure H_2O or D_2O, which largely facilitates the interpretation of the spectra. In the dilute gas, the wavenumber of the O-D vibration is 2720 cm^{-1}. In liquid water at room temperature, the absorption band maximum is positioned at about 2500 cm^{-1}. The strong wavenumber shift is attributed to hydrogen bonding in liquid water at ambient temperature. The large increase in molar integrated absorptivity by about an order of magnitude between gaseous and liquid-like states provides another measure for the strong intermolecular interactions in liquid water.

In the previous paper on the infrared absorption of concentrated aqueous LiCl-solutions, O-D spectra have been measured to 2800 bar and 350 °C and up to a maximum of 40 mole percent salt [10]. The analysis of the wavenumber data clearly indicates different kinds of intermolecular interactions at low and at high salt concentrations. The transition from "water-like" to "melt-like" behaviour occurs within a fairly narrow region between about 12 to 15 mole percent LiCl.

The purpose of the present paper is to investigate quantitatively the infrared absorption of the O-D stretching mode in $NaClO_4$-solutions to 20 mole percent salt and to pressures and temperatures of 2800 bar and 250 °C, respectively. In aqueous solutions containing perchlorate ions some peculiar

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effects in the field of nuclear magnetic resonance [11] and of infrared and Raman spectroscopy [12—15] have been observed: 1. The water proton relaxation rates strongly increase with perchlorate concentration. 2. In the fundamental and overtone vibrational spectra, the O-D bands are clearly split into two components, whereas the absorption contour in aqueous alkali halide solutions, as in pure HDO/H_2O, is only slightly asymmetric and has a rather simple shape with one maximum.

Experimental

The infrared spectra were measured with a high-pressure high-temperature cell described elsewhere [16]. The cell has only one window made from colourless synthetic sapphire. Details about the equipment and the experimental procedure are given in [10].

The spectra were recorded on a Perkin-Elmer 521 grating spectrometer which plots transmittance T versus wavenumber $\bar{\nu}$. The molar absorptivity $\varepsilon(\bar{\nu})$ is calculated from the relation:

$$\varepsilon(\bar{\nu}) = A(\bar{\nu})/C_{\mathrm{HDO}} \cdot l\,.$$

C_{HDO} is the concentration of HDO in moles per cubic meter, l is the optical path length in meters and $A(\bar{\nu}) = \log(T_0(\bar{\nu})/T(\bar{\nu}))$ is the absorbance. The transmittances, $T_0(\bar{\nu})$ and $T(\bar{\nu})$, are measured in independent runs: $T_0(\bar{\nu})$ is obtained with aqueous $NaClO_4$-solutions at the experimental temperature and pressure without HDO, and $T(\bar{\nu})$ is measured at the same conditions on solutions containing HDO.

The HDO-concentrations in the aqueous (6.4 mole% HDO in H_2O) salt solutions, presented in Table 1, are derived from PVT data of the corresponding $NaClO_4$-solutions in pure H_2O. These solution densities are obtained by interpolation from the experimental high-temperature high-pressure PVT data for water [17] including some data for solid $NaClO_4$ and some results for H_2O-$NaClO_4$ solutions at ambient temperature and pressure.

The calculations of $\varepsilon(\bar{\nu})$ have been performed on the BESM-4 at the Computer Center of the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. A band analysis using Gaussian components has been performed using a program developed by Gorbatyi's group [18]. The accuracy of the molar integrated absorptivity $B = \int \varepsilon(\bar{\nu})\,\mathrm{d}\bar{\nu}$ depends on the precise knowledge of

Table 1. Wavenumber $\bar{\nu}$(max) of the absorption maximum and molar integrated absorptivity B(O-D) of the O-D band in aqueous $NaClO_4$-solutions. T, P, and ϱ are the experimental temperature, pressure, and density.

T/°C	P/bar	ϱ/g cm^{-3}	$\bar{\nu}$(max)/ cm^{-1}	B(O-D)/ km mole^{-1}
	0 mole% $NaClO_4$			
25	10	1.000	2505	110.5
	1000	1.038	2502	111
	2800	1.096	2497	111
200	500	0.897	2572	61
	1000	0.924	2569	63
	2000	0.967	2568	67
	2800	0.995	2567	66.5
250	500	0.843	2589	50.5
	1000	0.877	2587	54
	2000	0.928	2583	54
	2800	0.959	2579	59
	5 mole% $NaClO_4$			
25	25	1.19	2507	96.7
200	500	1.075	2589	64
	1000	1.104	2577	63.4
	2000	1.148	2577	65.1
	2800	1.176	2567	66.9
250	500	1.015	2607	54.4
	1000	1.050	2607	55.7
	10 mole% $NaClO_4$			
25	25	1.348	2530	89.1
	2000	1.421	2522	91.4
200	500	1.228	2624	47.6
	1000	1.258	2632	49.8
	2000	1.302	2632	50.1
	2800	1.330	2627	53.9
250	500	1.164	2632	41.7
	1000	1.202	2632	44.9
	2000	1.255	2624	48.3
	2800	1.287	2622	47.8
	15 mole% $NaClO_4$			
25	25	1.486	2627	79.6
	2000	1.557	2627	83.7
200	500	1.364	2637	49.7
	1000	1.393	2632	50.4
	2000	1.435	2637	50.4
	2800	1.462	2637	53.4
250	500	1.297	2639	44.6
	1000	1.333	2637	45.6
	2000	1.385	2637	46.8
	2800	1.418	2637	49.9
	20 mole% $NaClO_4$			
25	25	1.608	2629	76
	2000	1.674	2629	80.7
200	500	1.484	2637	54.3
	1000	1.511	2639	49.7
	2000	1.550	2637	54.9
	2800	1.577	2637	54.3
250	500	1.414	2637	49.6
	2000	1.502	2637	53.9
	2800	1.531	2639	55.2

the HDO concentration, the PVT-data of the aqueous solutions, the measured transmittances, and the optical path length which was below 30 μm in most experiments. The accuracy of B(O-D), the molar integrated intensity of the O-D mode in HDO, is assumed to be better than $\pm 12\%$. The maxima of the O-D absorption bands are broad. This poses problems for a precise determination of $\bar{\nu}$(max), the wavenumber in the band maximum. $\bar{\nu}$(max) is assumed to be accurate within ± 4 cm^{-1}.

Results

The molar absorptivity ε of the O-D stretching mode of HDO in aqueous (6.4 mole% HDO in H_2O) $NaClO_4$-solution to a maximum of 20 mole% salt is shown for 25 °C and 25 bar in Figure 1. The spectrum of the pure (HDO/H_2O) solvent is given for comparison. With increasing salt concentration (Fig. 1), the O-D band maximum positioned at about 2500 cm^{-1} in HDO/H_2O shifts by 30 cm^{-1} toward higher wavenumbers and the molar integrated intensity of this band is diminished. Furthermore a high wavenumber component with maximum absorption at about 2635 cm^{-1} develops. The absorption contour is clearly split into two components. Within the limits of experimental accuracy, an isosbestic point seems to occur around 2590 cm^{-1}. The molar absorptivities in the maxima of both absorption components are in close quantitative agreement with Brink and Falk's infrared data on aqueous perchlorate solutions [19].

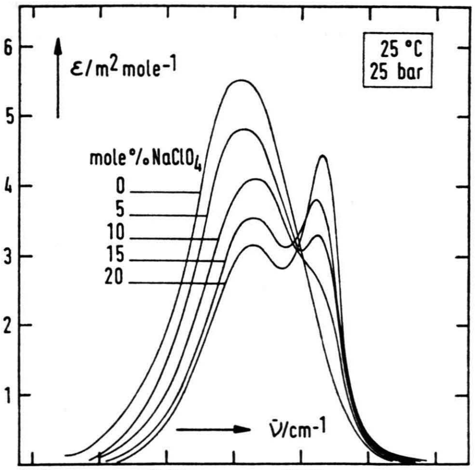

Fig. 1. Molar absorptivity ε/m^2 mole^{-1} of the O-D stretching mode of HDO in aqueous $NaClO_4$ solutions at 25 °C and 25 bar.

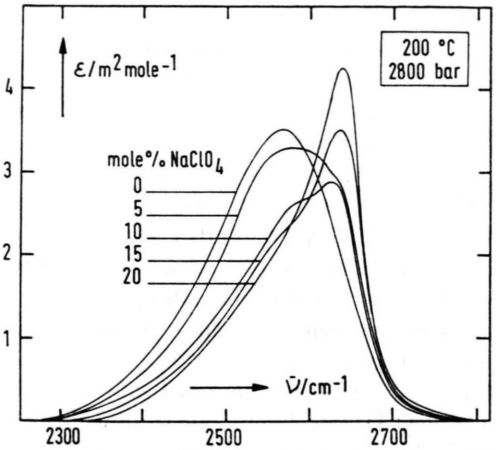

Fig. 2. Molar absorptivity ε/m^2 mole^{-1} of the O-D stretching mode of HDO in aqueous $NaClO_4$ solutions at 200 °C and 2800 bar.

In Fig. 2, the corresponding infrared spectra of the O-D stretching mode in aqueous $NaClO_4$-solutions at 200 °C and 2.8 kbar are shown. The intensity of the low wavenumber component is weaker and its absorption maximum is shifted to higher wavenumbers, as compared with room temperature data in Figure 1. The high wavenumber component, however, is not influenced by temperature variation: The maximum absorption occurs close to 2635 cm^{-1} and the molar absorptivity in the band maximum is 4.2 m^2 mole^{-1} for the 20 mole% $NaClO_4$ spectra in Figs. 1 and 2.

The experimental data for the position of the band maximum $\bar{\nu}$(max) and for the molar integrated absorptivity B measured on aqueous (HDO/H_2O) $NaClO_4$-solutions to a maximum salt concentration of 20 mole percent are summarized in Table 1.

Discussion

The interpretation of the vibrational spectra of aqueous electrolyte solutions suffers from the disadvantage that even the infrared and Raman spectra of pure water (or HDO/H_2O-mixtures) are still not fully understood. The spectroscopic work on aqueous electrolyte solutions in the far, middle, and near infrared has been reviewed by Verrall [20]. The spectra of the O-D stretching fundamental typically show broad structureless absorption bands. There are a few exceptions to this general type of behaviour: aqueous solutions with polyatomic anions of low proton affinity, such as ClO_4^-, BF_4^-, PF_6^-, and SbF_6^- show an additional high wavenumber component. The position of this rather narrow component is almost independent of the anion concentration. The variation of the spectra with perchlorate concentration, as in Fig. 1, demonstrates that the high wavenumber component is essentially due to the absorption of water molecules influenced by perchlorate ions whereas the low wavenumber component represents the absorption of the remaining bulk water.

In Fig. 3, the molar integrated absorptivity B(O-D) of the O-D stretching mode in aqueous perchlorate solutions which corresponds to the area below the $\varepsilon(\bar{\nu})$-spectra as in Figs. 1 and 2 is plotted versus the $NaClO_4$-concentration for three temperatures (25 °C, 200 °C, and 250 °C) at 0.5 kbar and 2 kbar. The addition of perchlorate to pure water lowers B(O-D). The effect is less pronounced at higher temperature. At 200 °C and 250 °C, within the limits of experimental accuracy, B(O-D) seems to be independent of concentration above 10 mole% $NaClO_4$. A mean value of B(O-D), calculated from the high-temperature data (200 °C and 250 °C) at 10 and 15 mole% $NaClO_4$, is 47.3 km mole^{-1}. A value of this size is found for pure high density water

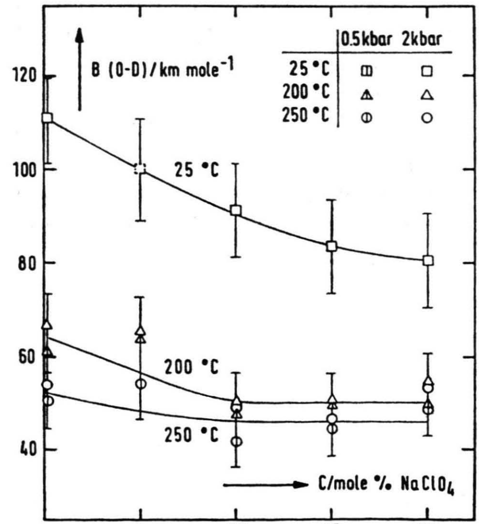

Fig. 3. Concentration dependence of the molar integrated absorptivity B(O-D)/km mole^{-1} of the O-D stretching mode of HDO in aqueous (HDO/H_2O)$NaClO_4$ solutions at temperatures of 25 °C, 200 °C, and 250 °C and pressures of 0.5 kbar and 2 kbar.

(HDO/H_2O) at higher temperatures close to the critical temperature (374 °C) [8], where hydrogen bonds have been shown to be of minor importance [21]. A comparison via the experimental B(O-D)-values thus suggests that water molecules in concentrated perchlorate solution are, if at all, only weakly (hydrogen) bonded at 200 °C.

The molar integrated absorptivities B(O-D) in sodium perchlorate solution differ from the corresponding data for LiCl-solutions where B(O-D) has been observed to increase with salt concentration [10]. Experimental intensity data for both systems at 200 °C are plotted versus the HDO-density, ϱ_{HDO}, in Figure 4. A few data points for pure water (HDO/H_2O) are included in Figure 4. With increasing LiCl-concentration, the molar integrated absorptivity B(O-D) is clearly enhanced. At 25 mole% LiCl, B(O-D) approaches the values observed in pure water at ambient temperature where water molecules are strongly interacting via hydrogen bonds. Increasing perchlorate concentration decreases B(O-D) to about 50 km mole^{-1}. These values are in close agreement with (hypothetical) pure water data as extrapolated along the dashed line in Figure 4. Since hydrogen bonded interactions are not important in pure water at elevated temperature and at moderate densities in the order of 0.6 g cm^{-3}, this agreement provides another indication of non-hydrogen-bonded interactions in concentrated perchlorate solutions at and above 200 °C.

Further support for the breakdown of hydrogen bonded interactions in aqueous perchlorate solu-

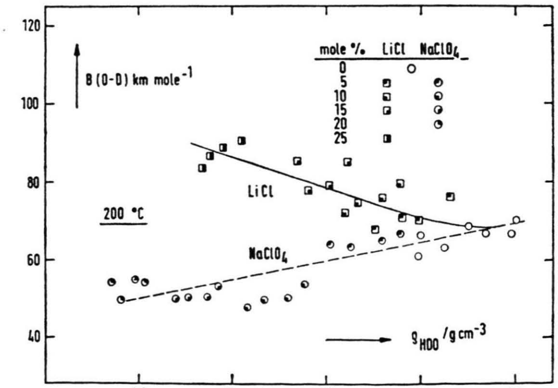

Fig. 4. Molar integrated absorptivity B(O-D)/km mole^{-1} of the O-D stretching mode of HDO in aqueous (HDO/H_2O) $NaClO_4$ and LiCl solutions at 200 °C plotted versus the HDO density ϱ_{HDO}.

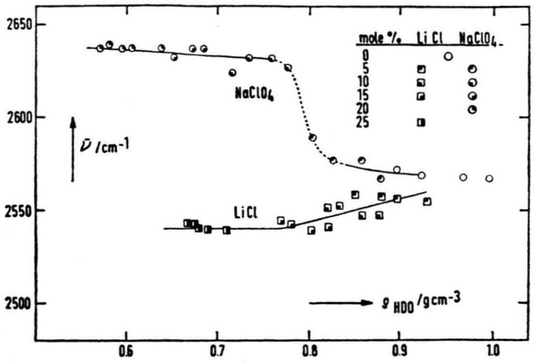

Fig. 5. Wavenumber $\bar{\nu}$(max)/cm^{-1} in the absorption band maximum of the O-D stretching mode of HDO in aqueous (HDO/H_2O) $NaClO_4$ and LiCl solutions at 200 °C plotted versus the HDO density ϱ_{HDO}.

tions results from the high value of $\bar{\nu}$(max), the position of the absorption band maximum of the O-D stretching mode in HDO. Data for 200 °C are presented in Figure 5. In pure water and in 5 mole% $NaClO_4$-solution, the O-D absorption band maximum is determined by the bulk water species whereas, toward higher perchlorate concentrations, the high wavenumber component around 2635 cm^{-1} constitutes the band maximum. With increasing LiCl-concentration, $\bar{\nu}$(max) shifts to lower values and approaches the corresponding room temperature data of $\bar{\nu}$(max) for LiCl- and $NaClO_4$-solutions at about 2530 cm^{-1}. The experimental observations for LiCl-solutions, an increase of B(O-D) (Fig. 4) and a decrease of $\bar{\nu}$(max), demonstrate the strong water-ion interactions in these solutions. The opposite type of behaviour, as measured on aqueous $NaClO_4$-solutions, proves the weak interactions between water molecules and surrounding perchlorate ions. The large differences in the vibrational band characteristics of concentrated aqueous $NaClO_4$- and LiCl-solutions are remarkable: The molar integrated absorptivities differ by a factor of two and the maximum wavenumbers differ by about 100 cm^{-1}. The quantitative theory of integrated intensities and wavenumber shifts in dense polar materials is still in an unsatisfactory stage. Thus the experimental observations can not be adequately discussed at present time.

The conclusions about the weak bonding in perchlorate solution are in complete agreement with previous results by Kecki [14] and by Walrafen [13] about the extensive breakdown of hydrogen-bonded water structure due to perchlorate ions. Furthermore Chizhik [22] derived from NMR relaxation data that ClO_4^--ions form extremely weak bonds with water molecules and thus carry no surrounding hydration sphere. These bonds may be identified as weak hydrogen bonds [23] or as non-hydrogen-bonded interactions. A clear distinction can not be made.

By computer analysis the experimental spectra have been resolved into three Gaussian components. The results for the molar integrated absorptivity B of the high wavenumber component with maximum absorption around 2635 cm^{-1} are given in Table 2 for 20 mole% $NaClO_4$. Within the limits of experimental accuracy, the component intensity B turns out to be independent of temperature and pressure (or density). The scattering of the data is probably due to the band separation procedure. The constancy of this component molar absorptivity is in satisfactory agreement with the observation that also the maximum wavenumber of this band is insensitive toward temperature and pressure variation (Figure 5). Both results establish that weakly bonded water molecules give rise to this band [21]. The high wavenumber component occurs also at lower temperatures and at smaller perchlorate concentrations as can be visualized by the computer band resolution. It is interesting to note that $\bar{\nu}$(max) of this band almost coincides with $\bar{\nu}$(max) of the high wavenumber component in the Raman spectrum of pure water (HDO/H_2O) measured to high pressures and temperatures [24]. Computer analysis of these scattering data revealed that, at high densities, $\bar{\nu}$(max) of the (Gaussian) high wavenumber component occurs close to 2635 cm^{-1} and is independent of temperature in an extended region from 25 °C to 400 °C. A high wavenumber component around 2630 cm^{-1} was also observed in the Raman spectra of aqueous KI solu-

T/°C	P/bar	B/km mole^{-1}
25	25	15.5
	2000	18.3
200	500	15.3
	1000	15.4
	2000	15.9
	2800	15.6
250	500	16.2
	2000	18.4
	2800	15.8

Table 2. Molar integrated absorptivity B of the high wavenumber component I of the O-D stretching mode in aqueous 20 mole% sodium perchlorate solution. (The data are derived from a computer band analysis.)

tions measured to high temperatures and pressures [24]. This coincidence in the infrared and Raman spectra of high-pressure high-temperature aqueous systems is important as interpretational uncertainties exist in literature which are due to the rather different appearance of Raman and infrared spectra measured on the same sample. The discrepancies are resolved if it is taken into account that the molar absorptivities for water molecules in different states are clearly different; hydrogen bonded species absorb about ten times as strongly as non-hydrogen-bonded water molecules. Thus if both kinds of water species are present, the hydrogen-bonded molecules dominate the absorption spectrum and give rise to a fairly symmetric band contour [8].

This argument has originally been made by Luck and Ditter [9] who measured the overtone absorption spectra and discussed the different appearance of fundamental and overtone HDO-spectra. The molar absorptivity of overtone and combination modes and the molar Raman scattering intensities seem to be rather similar for different kinds of water species. Thus speciation in the sample is directly reproduced by the vibrational overtone absorption and Raman scattering spectra.

The aqueous perchlorate solutions constitute an important spectroscopic system in that a non-continuous distribution of states is evident also from the O-D infrared spectrum. The ClO_4^--ion decreases the strength and thus the number of strong water-water interactions. The high molar absorptivity of these bonded HDO species is reduced simultaneously. As the HDO species influenced by perchlorate ions absorb at considerably higher wavenumbers, a band contour with clear indication of individual components results.

In the band analysis of the infrared and Raman spectra of the O-D stretching fundamental in pure water and aqueous solutions mostly three Gaussian components are used: a high wavenumber component I, a second component (II) which determines the O-D infrared absorption in water-rich systems, and a third component (III), mostly toward lower wavenumbers, which may be produced by deviations of the component bands from a true Gaussian shape. A band separation using three components has also been applied in the study of the corresponding overtone data [9]. The main features of the experimental spectra are described by means of the first two of these components. The results of a computer band separation for the O-D vibrational band in aqueous 20 mole% $NaClO_4$-solution at 250 °C and 2800 bar are illustrated in Figure 6. Component I occurs at 2642 cm^{-1}, component II at 2602 cm^{-1}, and component III at 2517 cm^{-1}. The assignment of component III is uncertain. The position of component II is remarkably close to the value of 2603 cm^{-1} which is extrapolated from Franck and Roth's data for pure water (HDO/H_2O) at 250 °C and 0.59 g cm^{-3} density [8, 25]. This hypothetical state is equivalent to the conditions as in Fig. 6, if the presence of $NaClO_4$ is neglected. All infrared perchlorate spectra as well as the pure water and solution Raman spectra [24] are reasonably well described by these three components where the main contributions are due to components I and II. They reflect the occurrence of loosely bound water species and bonded water species, respectively. An interpretation of the spectra in terms of a mixture of two discrete species, however, does not seem to be justified. The spectral characteristics, especially of component II, are drastically changed with temperature and pressure. Thus, at ambient temperature, component II refers to hydrogen-bonded species with maximum absorption at about 2500 cm^{-1} and high values of B(O-D) whereas, at

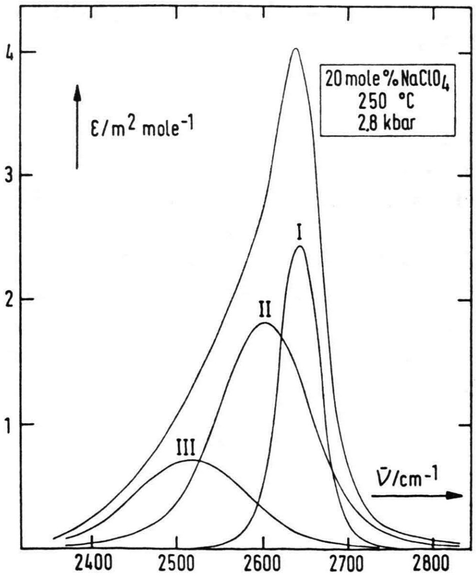

Fig. 6. Computer analysis of the infrared O-D stretching band of HDO in aqueous (HDO/H_2O) 20 mole% $NaClO_4$ solution at 250 °C and 2800 bar using three Gaussian components.

300 °C, component II refers to water molecules which are only weakly bound to one another. Their absorption has a maximum value close to 2600 cm^{-1}. The molar absorptivity is clearly reduced with respect to the room temperature data for the same component. These considerations demonstrate that a wide variety of states is contributing to the absorption of component II. The distribution of states giving rise to absorption component I seems to be rather narrow, as $\tilde{\nu}$(max) and the integrated molar absorptivity turn out to be insensitive to temperature and pressure variation. Even this component, however, does not refer to one well defined species of HDO-molecules as $\tilde{\nu}$(max) clearly depends on the specific solution under investigation. The infrared O-D vibrational spectra measured on the system water (HDO/H_2O)-carbon dioxide at high pressures and temperatures also show this high wavenumber component with maximum absorption, however, at about 2700 cm^{-1} [26]. From these observations it is concluded that each of the absorption components I and II refers to a distribution of states which seems to be especially broad for component II. The whole set of HDO infrared and Raman spectra measured on aqueous solutions or on pure water can probably be subdivided into components I and II (and perhaps a few more components). The occurrence of different kinds of water molecules which perform vibrational motions in at least two fairly limited frequency regions seems to be a general effect which has been obscured by the large molar absorptivity of component II.

The infrared spectra are not sufficient to characterize the states of water molecules which contribute to the individual absorption components. It has been assumed that water molecules located on a line between anion and cation give rise to the component I absorption [14]. The interpretation of recent NMR experiments by means of electrostatic relaxation theory yields a liquid structure with various kinds of water molecules vibrating at higher wavenumber. The qualitative explanation uses the concept of a "dielectric hole" [11].

In aqueous LiCl solutions between 12 and 15 mole% salt a transition from "water-like" to "melt-like" states appears to be indicated by the infrared absorption of the OD-stretching fundamental. A transition of this kind is not so evident from the $NaClO_4$-solution spectra. Apparently, temperature and concentration ranges are too limited. The concentration dependence, however, of the position of component II does, perhaps, provide a first indication that a transition of this kind does occur between 10 and 15 mole% $NaClO_4$ because, at 200 °C, its maximum shifts from 2570 cm^{-1} to 2600 cm^{-1} with increasing concentration. More convincing evidence may be derived from the Raman scattering of the Cl-O stretching mode of ClO_4^--ions in aqueous perchlorate solutions [27]. Changes are found only to 11 mole%. At higher concentrations, the water-ion interaction seems to remain unchanged. This observation is thus consistent with previous results [28] indicating that in aqueous solutions composed of monovalent ions a transition from "water-like" to "melt-like" states occurs between 10 and 15 mole% salt.

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