# Infrared Absorption of Concentrated Aqueous LiCl Solutions to High Pressures and Temperatures

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The infrared absorption of the O-D stretching fundamental of HDO in concentrated aqueous ($HDO/H_2O$) LiCl solutions to a maximum of 40 mole percent salt has been measured. 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 350 °C, respectively, are reported and discussed. Toward high salt concentrations, the dependence of $\bar{\nu}$(max) on temperature and on LiCl concentration decreases. The wavenumber data indicate a transition from "water-like" to "melt-like" behaviour at about 12 to 15 mole percent LiCl.

## Introduction

Concentrated aqueous electrolyte solutions receive increased interest for several reasons: The experimental investigation and theoretical description of fused salts has made considerable progress [1] and there is an obvious desire to develop a general treatment for ionic fluids from fused salts to concentrated and finally to diluted aqueous salt solutions. An improved understanding of such solutions is also important in geochemistry and for certain parts of power plant operation. The quantitative thermodynamic description of concentrated salt solutions using general solution theory has had good success [2]. Much more experimental facts are needed, however, and measurements at elevated temperatures and pressures obviously are particularly desirable in this context.

Apart from thermodynamic measurements, the determination of kinetic quantities as electrolytic conductance provides useful information. Conductance data up to about 600 °C and to high pressures and very high salt concentrations have been published by several groups (e. g. [3, 4]). Additional knowledge of other physical properties is necessary. A useful probe for structural phenomena is, among others, the absorption of the oxygen-hydrogen stretching mode of the water molecules. This absorption has been extensively investigated in the past [5 – 8]. It is also used in the present work. As in previous investigations, dilute solutions of HDO in $H_2O$ are used and the O-D vibration is studied. HDO is unsymmetric and the O-D absorption can easily be separated. In the dilute gas, the wavenumber of the vibrational transition is 2720 $cm^{-1}$; in liquid water at room temperature it is 2508 $cm^{-1}$. The reduction in wavenumber is attributed to hydrogen bonding, but can in part be caused by other intermolecular interactions. It is the purpose of this work, to investigate quantitatively and to discuss not only the position of the band maximum but also the absorptivity of the O-D stretching mode in LiCl-solutions to more than 25 weight percent salt and to 350 °C and 2.8 kbar.

## Experimental

The infrared spectra were measured with a high-pressure high-temperature cell described elsewhere [9]. The cell for operation to 3 kbar and 300 °C has only one window made from colourless synthetic sapphire. An optically flat stainless steel mirror inside the high pressure cell is pressed by a metal spring against the sapphire window from which it is separated by spacers of gold foil. These spacers determine the optical path length which, in the present investigation, was typically in the order of

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20 µm. The infrared beam passes through the sample layer twice: before and after reflection from the mirror. As the mirror is surrounded by the pressurized material on all sides, the optical path length is independent of pressure, if the bending of the sapphire window is neglected. This experimental technique which was introduced by Hare and Welsh [10] and improved by Franck and Roth [7] reduces the essential difficulty of quantitative absorption spectroscopy at high pressures and temperatures which relates to the problem of precisely knowing the optical path length.

The whole sample solution is contained within the high-pressure high-temperature cell. A stainless steel bellows inside the cell separates the solution from the pressurizing fluid (pure water). As pressure equilibrium is achieved by the bellows, the sample pressures are obtained from Bourdon gauges (Heise Bourdon Tube Co., Newton, Connecticut) in the pressurizing system at ambient temperature. The pressures are determined to ± 3 bar even at the highest pressures. The sample temperature is measured to better than ± 1 °C by means of a sheathed thermocouple, positioned close to the stainless steel mirror inside the high pressure cell.

Before each series of experiments the optical cell was flushed with pure water and carefully evacuated. Aqueous solutions up to concentrations of 25 mole percent LiCl were directly introduced into the optical cell. A 40 mole percent LiCl-solution was prepared, using an auxiliary high pressure vessel into which LiCl-solution and solid LiCl were introduced. After homogenization at about 250 °C, the solution was injected from the auxiliary high pressure vessel into the optical cell. The infrared spectra of the O-D stretching mode of HDO diluted in aqueous LiCl-solutions 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:

$$\varepsilon(\bar{\nu}) = A(\bar{\nu})/C_{\mathrm{HDO}} \cdot l . \qquad (1)$$

$A(\bar{\nu}) = \log(T_0(\bar{\nu})/T(\bar{\nu}))$ is the absorbance, $C_{\mathrm{HDO}}$ is the concentration of HDO in moles per cubic meter and $l$ is the optical path length in meters. The transmittances $T_0(\bar{\nu})$ and $T(\bar{\nu})$ are measured in independent runs; $T_0(\bar{\nu})$ is obtained with aqueous LiCl-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-concentration of the aqueous (6.4 mole% HDO in $H_2O$) salt solutions is derived from the PVT data of the corresponding LiCl-solutions in pure $H_2O$. PVT-data for pure water are taken from the experimental work of Hilbert, Tödheide, and Franck [11]. The density of the LiCl-solutions is obtained by interpolation of the experimental data published by Egorov, Zarembo, and Federov [12] and by Hwang, Lüdemann, and Hartmann [3]. Approximate PVT-data for the 40 mole% LiCl solutions were obtained by an interpolation procedure including density data for molten LiCl.

The optical path length $l$ is determined by calibration with a reference substance of known molar absorptivity. 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. The accuracy of the molar integrated absorptivity $B = \int \varepsilon(\bar{\nu}) \mathrm{d}\bar{\nu}$ depends on the precise knowledge of the HDO concentration, the PVT-data of the aqueous solutions, the optical path length, and the measured transmittances. It is assumed to be better than ± 10%. The maxima of the O-D stretching bands are rather broad. This makes the determination of the wavenumber in the band maximum, $\bar{\nu}$(max), less precise. The values are assumed to be accurate within $\pm 4\ \mathrm{cm}^{-1}$.

## Results

The molar absorptivity $\varepsilon$ of the O-D stretching mode of HDO (6.4 mol% in $H_2O$) in 2 mole percent aqueous LiCl-solution is shown in Fig. 1 for 200 °C, 250 °C, 300 °C, and 350 °C at a constant pressure of 2800 bar. The corresponding spectrum (2 mol% LiCl-solution) at 25 °C and 25 bar is given for comparison. The molar integrated absorptivity $B$ which is the area below the $\varepsilon$ versus $\bar{\nu}$ curves clearly decreases with increasing temperature, while the position of the absorption band maximum, $\bar{\nu}$(max), shifts toward higher wavenumbers. From 200 °C to 350 °C, $\bar{\nu}$(max) increases by about $32 \pm 4\ \mathrm{cm}^{-1}$ (Figure 1).

In Fig. 2, the molar absorptivity of HDO in 25 mol percent aqueous LiCl-solution is plotted for the same pressures and temperatures as in Figure 1. The appearance of the spectra in Figures 1 and 2 is similar: the absorption curves have a rather simple shape with one maximum and are only

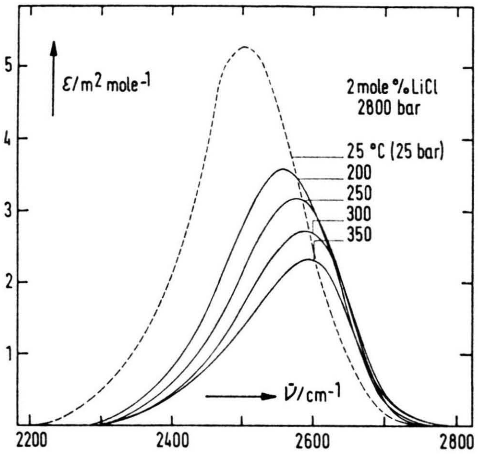

Fig. 1. Molar absorptivity $\varepsilon$ of the O-D stretching mode of HDO in 2 mole percent aqueous LiCl solution at 2800 bar and temperatures between 200 °C and 350 °C. The dashed line gives the corresponding spectrum at 25 °C and 25 bar.

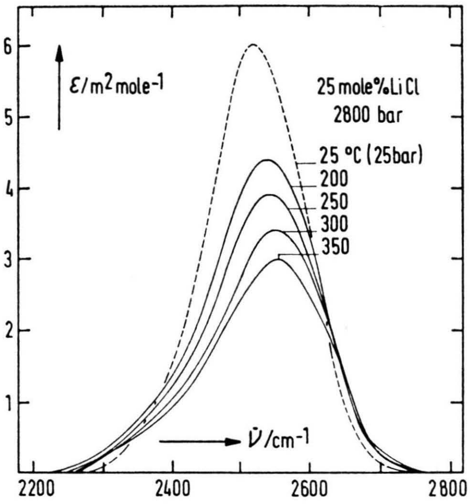

Fig. 2. Molar absorptivity $\varepsilon$ of the O-D stretching mode of HDO in 25 mole percent aqueous LiCl solution at 2800 bar and temperatures between 200 °C and 350 °C. The dashed line gives the corresponding spectrum at 25 °C and 25 bar.

slightly asymmetric. At identical pressure and temperature, the molar integrated absorptivity of the concentrated LiCl-solution (Fig. 2) exceeds the value measured with the 2 mol percent LiCl-solution (Figure 1). Closer inspection of the data in Figs. 1 and 2 demonstrates the "blue-shift" of the band maximum with increasing temperature being less pronounced at higher LiCl-concentration.

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

| $T$/°C | $P$/bar | $\varrho$/g cm$^{-3}$ | $\tilde{\nu}$(max)/cm$^{-1}$ | $B$/km mol$^{-1}$ |
|---|---|---|---|---|
| | 0% LiCl | | | |
| 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 |
| 300 | 500 | 0.777 | 2603 | 43 |
| | 1000 | 0.823 | 2599 | 44.5 |
| | 2000 | 0.885 | 2594 | 47 |
| | 2800 | 0.922 | 2592 | 47 |
| 350 | 500 | 0.694 | 2613 | 33.5 |
| | 1000 | 0.763 | 2610 | 37 |
| | 2000 | 0.840 | 2604 | 40.5 |
| | 2800 | 0.882 | 2601 | 43.5 |
| | 2 mole% LiCl | | | |
| 25 | 25 | 1.023 | 2507 | 106 |
| 200 | 500 | 0.926 | 2565 | 64 |
| | 1000 | 0.953 | 2566 | 67.5 |
| | 2000 | 0.988 | 2562 | 66.5 |
| | 2800 | 1.010 | 2562 | 69.5 |
| 250 | 500 | 0.881 | 2583 | 55.5 |
| | 1000 | 0.911 | 2583 | 57.5 |
| | 2000 | 0.958 | 2579 | 61 |
| | 2800 | 0.988 | 2577 | 61 |
| 300 | 500 | 0.815 | 2595 | 46 |
| | 1000 | 0.863 | 2592 | 44.5 |
| | 2000 | 0.918 | 2590 | 51 |
| | 2800 | 0.956 | 2588 | 53 |
| 350 | 1000 | 0.808 | 2599 | 45.5 |
| | 2000 | 0.878 | 2597 | 48 |
| | 2800 | 0.922 | 2594 | 45.5 |
| | 5.23 mole% LiCl | | | |
| 25 | 25 | 1.062 | 2507 | 107 |
| 200 | 300 | 0.967 | 2558 | 67.5 |
| | 1000 | 1.000 | 2557 | 71 |
| | 1600 | 1.020 | 2556 | 70 |
| | 2800 | 1.058 | 2554 | 76.5 |
| 250 | 300 | 0.924 | 2572 | 58 |
| | 1000 | 0.963 | 2569 | 61.5 |
| | 1600 | 0.988 | 2568 | 62 |
| | 2800 | 1.035 | 2567 | 64.5 |
| 300 | 300 | 0.865 | 2584 | 49.5 |
| | 1000 | 0.917 | 2583 | 50 |
| | 1600 | 0.948 | 2582 | 52 |
| | 2800 | 1.005 | 2577 | 55 |

Table 1 (continued 1).

| $T$/°C | $P$/bar | $\varrho$/g cm$^{-3}$ | $\bar{\nu}$(max)/cm$^{-1}$ | $B$/km mol$^{-1}$ |
|---|---|---|---|---|
| 350 | 300 | 0.807 | 2593 | 39.5 |
| | 1000 | 0.871 | 2592 | 43.1 |
| | 1600 | 0.909 | 2592 | 46 |
| | 2800 | 0.979 | 2588 | 48 |
| | 10 mole% LiCl | | | |
| 25 | 25 | 1.118 | 2515 | 111 |
| 200 | 500 | 1.045 | 2551 | 72.5 |
| | 1000 | 1.062 | 2552 | 74.5 |
| | 2000 | 1.094 | 2547 | 76 |
| | 2800 | 1.119 | 2547 | 79.5 |
| 250 | 500 | 1.010 | 2558 | 68.5 |
| | 1000 | 1.029 | 2555 | 65.5 |
| | 2000 | 1.066 | 2552 | 65.5 |
| | 2800 | 1.099 | 2553 | 65.5 |
| 300 | 500 | 0.967 | 2568 | 54.5 |
| | 1000 | 0.990 | 2567 | 55 |
| | 2000 | 1.034 | 2563 | 58.5 |
| | 2800 | 1.069 | 2564 | 60 |
| 350 | 500 | 0.923 | 2580 | 47.5 |
| | 1000 | 0.951 | 2577 | 48.5 |
| | 2000 | 1.003 | 2573 | 50.5 |
| | 2800 | 1.045 | 2573 | 49.5 |
| | 15 mole% LiCl | | | |
| 25 | 20 | 1.173 | 2520 | 113.5 |
| 200 | 500 | 1.105 | 2544 | 85.5 |
| | 1000 | 1.120 | 2542 | 78 |
| | 2000 | 1.153 | 2539 | 79 |
| | 2800 | 1.180 | 2541 | 85 |
| 250 | 500 | 1.076 | 2547 | 69 |
| | 1000 | 1.092 | 2548 | 71 |
| | 2000 | 1.125 | 2545 | 72 |
| | 2800 | 1.151 | 2547 | 74 |
| 300 | 500 | 1.039 | 2556 | 60.5 |
| | 1000 | 1.060 | 2553 | 61 |
| | 2000 | 1.097 | 2552 | 63.5 |
| | 2800 | 1.127 | 2552 | 64.5 |
| 350 | 500 | 1.003 | 2562 | 52.5 |
| | 1000 | 1.026 | 2562 | 54 |
| | 2000 | 1.067 | 2559 | 56 |
| | 2800 | 1.099 | 2557 | 58.5 |
| | 25 mole% LiCl | | | |
| 25 | 25 | 1.281 | 2522 | 108.5 |
| 200 | 500 | 1.219 | 2543 | 83 |
| | 1000 | 1.231 | 2542 | 86.5 |
| | 2000 | 1.260 | 2539 | 88.5 |
| | 2800 | 1.293 | 2539 | 90.5 |
| 250 | 500 | 1.192 | 2544 | 76.5 |
| | 1000 | 1.206 | 2544 | 79 |
| | 2000 | 1.232 | 2543 | 80.5 |
| | 2800 | 1.256 | 2542 | 80 |

Table 1 (continued 2).

| $T$/°C | $P$/bar | $\varrho$/g cm$^{-3}$ | $\bar{\nu}$(max)/cm$^{-1}$ | $B$/km mol$^{-1}$ |
|---|---|---|---|---|
| 300 | 500 | 1.166 | 2553 | 66.5 |
| | 1000 | 1.179 | 2549 | 67.5 |
| | 2000 | 1.204 | 2549 | 70 |
| | 2800 | 1.227 | 2548 | 71.5 |
| 350 | 500 | 1.139 | 2559 | 60 |
| | 1000 | 1.154 | 2554 | 61.5 |
| | 2000 | 1.180 | 2553 | 62 |
| | 2800 | 1.203 | 2552 | 65 |
| | 40 mole% LiCl | | | |
| 250 | 500 | 1.322 | 2549 | 83.5 |
| | 1000 | 1.333 | 2548 | 86.5 |

The experimental data for the position of the band maximum $\bar{\nu}$(max) and for the molar integrated absorptivity $B$ measured with aqueous ($HDO/H_2O$) LiCl-solution to a maximum concentration of 40 mole percent are summarized in Table 1.

## Discussion

The interpretation of the infrared spectra of concentrated electrolyte solutions must remain qualitative, since even the treatment of the absorption of pure water is still not satisfactory. New approaches in the determination of correlation functions and computer simulations may be promising. At present, however, most discussions still use the simplified "mixture" or "continuum" models and the concept of "structure breaking" and "structure making" influences [13]. The electrolyte solutions show broad absorptions containing limited information. Some solutions of polyatomic ions, as perchlorate and tetrafluoroborate, show an additional high-wavenumber component of the OH- or OD-stretching mode [14]. Spectroscopic work in the far, middle, and near infrared regions has been reviewed by Verrall [15]. Almost all experiments have been made at or near ambient pressure and temperature and the results refer mainly to the position of the band maxima. Few data are available on the integrated molar absorptivity. The attention focuses on the oxygen-hydrogen bond which is often studied via the absorption of the OD-stretching mode of HDO diluted in $H_2O$. The influence of cations on this band appears to be weaker than that of anions. High concentrations of $ClO_3^-$- and $J^-$-ions, for example, shift this band by 50 cm$^{-1}$ to higher wavenumber relative to pure water. This is interpreted qualitatively as being due to a weakening of hydrogen bonds ("structure breaking" effect). Some carbonic acid anions, however, produce the opposite effect: a shift of up to 30 cm$^{-1}$ to lower values. Chloride ions as in LiCl solutions show an intermediate type of behaviour.

The shift of maximum wavenumber as a function of LiCl concentration for several temperatures at constant high pressure of 2.8 kbar is shown in Figure 3. The isotherm at 25 °C is for low pressures between 10 and 25 bar. The wavenumber increase of nearly 100 cm$^{-1}$ for pure water is essentially due to the temperature increase, since the water density at 200 °C and 2800 bar is 0.99 g cm$^{-3}$ and is only about 10 percent lower at 350 °C. The variation of $\bar{\nu}$(max) caused by these temperature changes in pure water is much higher than that produced by the addition of LiCl to liquid water. The strong temperature dependence of $\bar{\nu}$(max) is characteristic for hydrogen bonded interactions ("water-like" behaviour); in polar fluids without hydrogen bonds, such as hydrogen chloride [16] and ammonia [17], only minor changes of $\bar{\nu}$(max) due to temperature variation are observed.

Two further interesting conclusions can be derived from Fig. 3 if one accepts the qualitative terms of the making and breaking of water structure: At 25 °C the added salt produces a slight high wavenumber shift and possibly a certain decreased degree of structure. At 200 °C and above, however, pure water is already much less structured and the added LiCl appears to increase some kind of structure. Thus there is an intermediate temperature around 100 °C where these two effects nearly compensate. The second remarkable observation is that above about 15 mole percent LiCl the concentration dependence of $\bar{\nu}$(max) nearly disappears and the temperature dependence becomes small. The two data for the 40 mole percent solution in Table 1 support the observation of diminishing concentration dependence. Thus above 15 mole percent the fluid begins to behave in a melt-like way. It is suggested that $\bar{\nu}$(max) for modest amounts of water dissolved in fused LiCl is close to the values at the high concentrations of the isotherms of Figure 3. Accordingly, the wavenumber shift of the O-D-band from the high gas phase value to the region around 2540 cm$^{-1}$ should mainly be produced by the interaction of ions with water molecules rather than by the association of water species. The temperature and concentration dependence of $\bar{\nu}$(max) being strong at LiCl concentrations up to about 12 mole percent and rather weak toward higher concentrations, thus seems to favour a subdivision of aqueous solutions with different amounts of salt in "water-like" or "melt-like" regimes. These conclusions agree with previous results on different kinds of water-salt systems which show fairly narrow transition regions between water-like and melt-like behaviour [18]. The concentration region where this transition takes place mainly depends on the ion charges. For monovalent ions as in the LiCl-situation, the transition occurs at salt concentrations of about 12 to 15 mole percent.

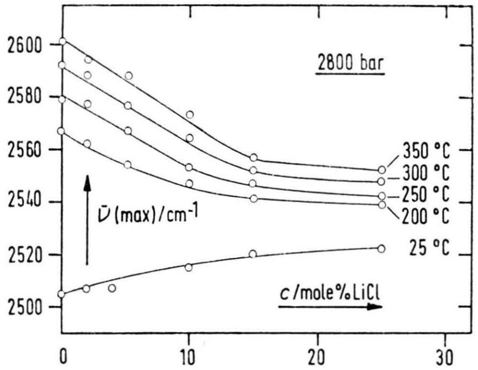

Fig. 3. Concentration dependence of the O-D band maximum, $\bar{\nu}$(max), in aqueous (HDO/$H_2O$) LiCl solution at 2800 bar for 200 °C, 250 °C, 300 °C, and 350 °C. The isotherm for 25 °C refers to pressures between 10 bar and 25 bar (see Table 1).

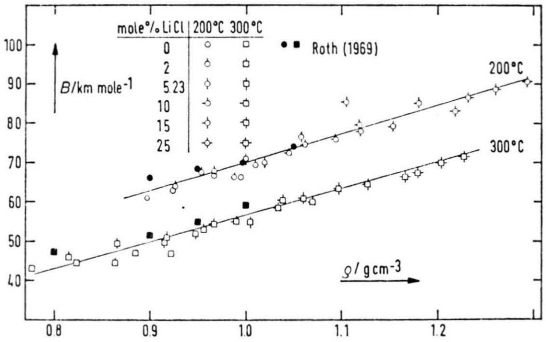

Fig. 4. Density dependence of the molar integrated absorptivity *B* of the O-D stretching mode in aqueous (HDO/$H_2O$) LiCl solution at 200 °C and 300 °C. The literature data are from Ref. [19].

The behaviour of the molar integrated absorptivity $B$ is demonstrated in Figure 4. Two isotherms for 200 °C and 300 °C of $B$ as a function of the overall solution density $\varrho$ in gcm$^{-1}$ are shown. The diagram includes values for pure water obtained and published previously [7, 19]. The agreement between the old and new data is good. The data points for one concentration and one temperature belong to different pressures which can be found from Table 1. It is evident from Fig. 4 that increasing compression as well as increasing salt concentration enhance the absorptivity. Contrary to $\bar{\nu}$(max) (see Fig. 3), the absorptivity does not show a significant change in temperature dependence toward high salt concentrations. The approach to a "melt-like" character thus is not observable from the $B$-values in Figure 4. It is perhaps surprising, that the increases in molar integrated absorptivity produced by pressure or by dissolved salt exhibit the same linear dependence on the overall density within the investigated region. This may, however, be fortuitous. If other scales of density are chosen, each isotherm of Fig. 4 is split into several straight lines. The linearity of the two isotherms suggests the similarity between the influences of Li$^+$- and Cl$^-$-ions and neighboring water molecules on the absorptivity of the O-D mode.

In previous infrared studies with pure polar fluids such as water [7] and hydrogen chloride [16] the molar integrated absorptivity $B$ and the maximum wavenumber $\bar{\nu}$(max) for one particular H-X-stretching mode were plotted versus one another and nearly linear relationships were obtained. Figure 5 shows such a diagram for the lithium chloride solutions. Straight lines are found here also, but the slope varies according to concentration. Above 15 mole percent, however, the slope variation appears to become negligible, perhaps another indication of a transition toward a "melt-like"-character of the fluid. Unfortunately the theory of integrated absorptivities of dense polar fluids and mixtures is still in its infancy. Reliable modern experimental data are scarce and should be increased. High-pressure high-temperature infrared absorption measurements with concentrated aqueous alkali perchlorate solutions which show a more structured absorption contour have been started [20].

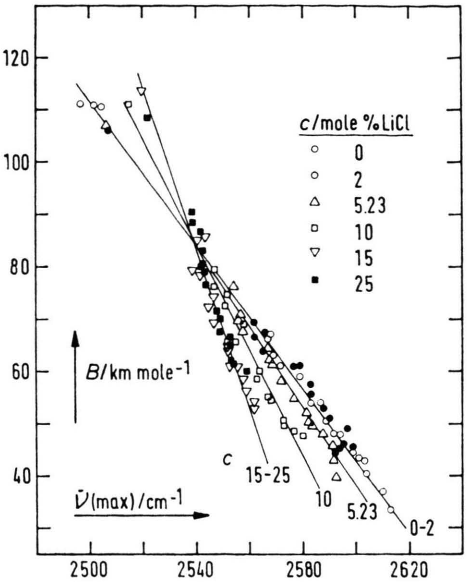

Fig. 5. Molar integrated absorptivity $B$ plotted versus the wavenumber $\bar{\nu}$(max) in the band maximum for the O-D stretching mode of HDO in concentrated aqueous LiCl solutions at high pressures and temperatures.

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