Temperature Coefficient of the Refractive Index of H$_2$O and D$_2$O and Proposed Models of Water Structure

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The temperature coefficient of the refractive index, ($\frac{dn}{dT}$)$_p$, has been measured for deuterium oxide. The observed values are considered together with those previously obtained for water. The experimental data cannot be explained with the best known models of molecular polarizability, at least in the approximation generally used in these models. Therefore they are discussed on the basis of a different approximation, suggested by a well-known structural model of liquid water. It is shown that the experimental results are very well explained, in a wide range of temperature, with the hypothesis of the existence of “structural voids”.

1. Introduction

In a previous paper [1], some of the best known models of molecular polarizability were tested on the basis of very accurate measurements of ($\frac{dn}{dT}$)$_p$ ($n =$ refractive index) of water and organic liquids. The Lorentz-Lorenz (L-L), Onsager-Böttcher (O-B), Kirkwood [2] and Omini [3] models were examined, and their abilities to fit the experimental data were compared. In these models the concept of local field, originating in the difference of the electric field intensity acting on a polarizable molecule in the liquid and in the gaseous phases, has been applied to describe the density dependence of the dielectric constant.

It is worthwhile noting that in the formalism of the L-L relation for spherical molecules there is only one free parameter, while in the O-B relation we have an additional “size parameter”, and other shape parameters appear in the formulae for ellipsoidal molecules. The graphical methods, which are generally used, may show an apparent superiority of the formulae containing more than one parameter merely because of the extra degrees of freedom available for fitting the data. For this reason we used numerical tests, in which the parameters are fixed “a priori”.

In this paper we go further in our analysis by presenting, together with the experimental data concerning the refractive index of D$_2$O, some satisfactory results in our attempt to find a model consistent with the behaviour of the refractive index of water and deuterium oxide.

2. Experimental Results

Our experimental setup, which is described in detail elsewhere [4], is a very sensitive interferometer. With its aid, we are able to measure ($\frac{dn}{dT}$)$_p$ with an accuracy of $10^{-7}$ K$^{-1}$. A number of measurements of ($\frac{dn}{dT}$)$_p$ for some liquids, particularly for water, is given in references [1] and [4].

Recently, to increase the number of experimental data available for our purpose of investigating the anomalous behaviour of water, we have performed measurements of ($\frac{dn}{dT}$)$_p$ for D$_2$O in the whole range (275.15 K, 353.15 K). The experimental points are shown in Fig. 1 together with the line representing the best fit of these points which is obtained by an empirical formula containing two free parameters, viz.

$$
\left( \frac{dn}{dT} \right)_p = A_0 \left( \frac{\exp \frac{K}{T} - \exp \frac{K}{T_0} }{T} \right).
$$

Equation (1) has been found to be very suitable for the fit of these data and those previously obtained for light water (dashed line in Figure 1). The respective values of the parameters and their standard errors are given in Table 1 where $T_0$ is the temperature at which ($\frac{dn}{dT}$)$_p$ vanishes.

From the reported results, we conclude that there is no evidence for any discontinuous behaviour, while it appears to be unquestionable that the high-temperature limit of ($\frac{dn}{dT}$)$_p$ for water and deuterium oxide coincide.

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Our results suggest that all the tested models are quite inadequate for water since remarkable deviations are observed. Furthermore, the deviations shown by the L-L and O-B spherical models have the same order of magnitude and the same temperature dependence [1]. More recently, the same computations have been performed by us for D_2O with similar results. This fact suggests that the O-B correction in the L-L relation is in this case really negligible and cannot explain the observed deviations which might be ascribed to molecular interactions completely neglected by the tested theories. The deviations shown by the other liquids examined, however, are generally very small, the O-B formula being able to fit the data within the experimental error, or nearly so.

To explain the deviations of the observed values from those given by the Onsager relation, a corrective factor taking into account the orientational molecular correlations, due to the characteristic short-range order of liquids, is introduced in the Kirkwood theory of dielectric constant [5]. In order to calculate this factor, water is treated as an associated liquid and the tetrahedral coordination model proposed by Bernal and Fowler is employed. The corrective factor, however, only concerns the orientational polarizability which is negligible in the optical range. The term related to the induced dipole moment, more specifically to the refractive index at the optical frequencies, is treated in an approximate way starting from the O-B relation and making some arbitrary simplifications. Yet the different approximation, involving this term, causes the O-B and Kirkwood relations to be hardly comparable. Therefore, the problem of evaluating the possible influence of the nearest-neighbour interactions on the dielectric constant of water is very difficult even if, as Hill pointed out [6], it seems quite probable that the dielectric constant is slightly affected by association.

At present there are no theories giving evidence for the specific dependence of the refractive index

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**Table 1. Values of the parameters**

<table>
<thead>
<tr>
<th></th>
<th>( A_0 ) [K(^{-1})]</th>
<th>( \sigma_{A_0} )</th>
<th>( K ) [K]</th>
<th>( \sigma_K )</th>
<th>( T_0 ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2O</td>
<td>0.250 ( \times 10^{-5} )</td>
<td>0.005 ( \times 10^{-5} )</td>
<td>1.330 ( \times 10^3 )</td>
<td>0.005 ( \times 10^3 )</td>
<td>275.15</td>
</tr>
<tr>
<td>D_2O</td>
<td>0.200 ( \times 10^{-5} )</td>
<td>0.005 ( \times 10^{-5} )</td>
<td>1.435 ( \times 10^3 )</td>
<td>0.005 ( \times 10^3 )</td>
<td>281.65</td>
</tr>
</tbody>
</table>
on molecular interactions. On the other hand, the experimental data given in the literature and the present work seem to indicate such influences to be practically negligible. With the exceptions of water and deuterium oxide, \((\partial n/\partial T)_p\) is nearly constant for all the tested liquids whether they associate or not.

If we agree to this point of view and remain within the classical models without appealing to the dependence of the molecular polarizability upon the environment, we must conclude that the classical relations are formally inadequate since the temperature- and pressure-dependence of the refractive index is assumed merely via density. Generally, the comparison of the derivative of the refractive index with respect to the density at constant temperature with the derivative at constant pressure is not very satisfactory; this fact confirms that the assumption above is really inadequate [7].

The O-B formula is the only relation that, making eventually different assumptions, can give an account of the experimental results. This relation may be rewritten in the form

\[
\frac{n^2 - 1}{12 \pi n^2} = \chi \left\{ \frac{1}{2} (2 n^2 + 1) - \frac{8}{3} \pi \chi (n^2 - 1) \frac{1}{\varphi} \right\}
\]

where \(\chi\) is the polarizability, independent of the temperature, of the isolated molecule. In this way the refractive index is a function not only of the number density \(\varphi = N/V\) but also of the volume fraction \(\varphi = (4/3) \pi a^3 N/V\) occupied by the molecules, \(a\) being a parameter identified with the molecular radius. The relation, however, is used setting: i) \(\varphi = 1\) or ii) \(a = \text{const}\), that is \(\varphi = K N/V\); in the first case we have the Onsager approximation leading back to the L-L relation; the second case corresponds to the Böttcher approximation that we used previously [1]. The two positions are totally reverse but lead to the same result, that is to the dependence of the refractive index merely upon the density. To make a different choice of \(\varphi\), we must consider that this quantity is essentially determined by the “structure” assigned to the system. Therefore it is useful to refer to those structural models that best fit the thermal behaviour of water. It results from the analysis of these models that \(\varphi = 1\) is generally used. The exceptions refer to the models involving “structural voids”: the so-called “interstitial models” provide the best example of this kind.

In order to simplify the following discussion, we will deduce directly a relation suitable for describing \(n\) in a system as hypothesized by an interstitial model. We will show later that the same result could be obtained using the Onsager theory.

3. The Refractive Index in an Interstitial Model

The employment of an interstitial model implies the refractive index to be calculated for a fluid in which there are holes, partially filled by the molecules of the same fluid. Consider a fluid, for the sake of simplicity, to consist of a continuum medium with only spherical holes. In the first approximation, the calculation may be carried out in the following way. Consider a large spherical specimen, of refractive index \(n_0\), in an impolarizable container of radius \(R\). If \(E_0\) is the field intensity when the sphere is not present, \(E\) the uniform part of the field intensity inside the sphere, and \(m'\) the moment for the whole sphere, we have from electrostatics that [2]

\[
E = \frac{3}{n_0^2 + 2} E_0, \tag{2}
\]

\[
m' = \frac{n_0^2 - 1}{n_0^2 + 2} E_0 R^3. \tag{3}
\]

We now introduce in the dielectric, in such a way that \(p\) and \(T\) are maintained constant, a single spherical hole of radius \(r\), for which, in the given environment

\[
m = -\frac{n_0^2 - 1}{2 n_0^2 + 1} r^3 E = \chi E, \tag{4}
\]

where \(E\) is the field intensity when the hole is not present. Then (2) and (3) become [2]

\[
E = \frac{1}{n_0^2 + 2} \left[ 3 E_0 - 2 (n_0^2 - 1) \frac{\chi}{R^3} E \right], \tag{5}
\]

\[
m' = \frac{1}{n_0^2 + 2} \left[ (n_0^2 - 1) E_0 R^3 + 3 n_0^2 \chi E \right]. \tag{6}
\]

If (5) is solved with respect to \(E\), to the first order in \(\chi\), and the result is substituted in (6), one finds

\[
\Delta m' = \frac{9 n_0^2}{(n_0^2 + 2)^2} \chi E_0 \tag{7}
\]

for the change in total moment of the specimen.
Differentiation of (3) gives the corresponding variation of the refractive index:

$$\Delta n_0 = \frac{(n_0^2 + 2)^2}{6 n_0} \frac{\Delta m'}{E_0 R^3}.$$  (8)

Substitution of (7) in (8) yields

$$\Delta n_0 = 3 \frac{n_0}{2} \frac{n_0^2 - 1}{R^3}$$  (9)

and finally introducing in (9) the value of $\alpha$ given by (4) one gets

$$\Delta n_0 = -\frac{3}{2} \frac{n_0(n_0^2 - 1)}{2n_0^2 + 1} \frac{r^3}{R^3}.$$  (10)

In addition, we will suppose that an occupied hole does not give a contribution to $\Delta n_0$, i.e. it is externally equivalent to a hole uniformly filled by the medium with refractive index $n_0$. This is clearly the case if the hole and the molecule sizes match quite well. In general, this result follows as a first approximation when the molecule in the hole is considered as an isolated molecule, i.e. neglecting the electrostatic interactions with the medium.

Consider again Equation (10). If $V_e$ is the volume of the hole and $V$ the total volume of the system, the variation induced by $N_1$ holes is given by the relation

$$\Delta n_0 = -\frac{3}{2} \frac{n_0(n_0^2 - 1)}{2n_0^2 + 1} \frac{V_e}{V} N_1.$$  (11)

which represents the variation of the refractive index following either the addition of $N_1$ holes to a continuous medium or the ejection of $N_1$ molecules from as many occupied holes. In the latter case, $n_0$ should indicate the refractive index of an hypothetical reference system in which all the holes are occupied.

The validity of (11) is confirmed by the equation

$$\Delta \varepsilon_2 = N_0 \left( \frac{1}{3} V_0 \varepsilon_2 (\varepsilon_0 - \varepsilon_2) + \sum_{s}^{1-3} \frac{1}{\varepsilon_s + D_s(\varepsilon_0 - \varepsilon_2)} \right)$$  (12)

which is a modification of the Ross and Sack equation [8] obtained for a solution of an apolar solute in apolar solvent using the Onsager theory. $\varepsilon_2$ and $\varepsilon_0$ are the dielectric constant of the solvent and solute, respectively, $N_0$ the number of solute molecules per unit volume, and $V_0$ the volume of the solute molecule. The two equations match quite well for $\varepsilon_0 = 1$ and $D_1 = D_2 = D_3 = 1/3$ (spherical holes).

If the O-B relation is applied to the reference fluid, with refractive index $n_0$, then taking its derivative with respect to temperature yields

$$\frac{1}{A_{op}} \left( \frac{\partial n_0}{\partial T} \right)_p = -\frac{3}{2} \frac{n_0(n_0^2 - 1)}{2n_0^2 + 1}$$

where $A_{op}$ is the thermal expansivity of the reference system and $\varphi$ the volume fraction occupied by the molecules. If we take into account the assumptions concerning the occupied holes, then we may set $\varphi = 1$ in the reference system so that

$$\frac{1}{A_{op}} \left( \frac{\partial n_0}{\partial T} \right)_p = -\frac{3}{2} \frac{n_0(n_0^2 - 1)}{2n_0^2 + 1}.$$  (13)

Thus (11) becomes

$$n - n_0 = \frac{1}{A_{op}} \left( \frac{\partial n_0}{\partial T} \right)_p \frac{\Delta V}{V}.$$  (14)

where $\Delta V = V_e N_1$ has been used. If the possible temperature dependence of the

$$\frac{1}{A_{op}} \left( \frac{\partial n_0}{\partial T} \right)_p$$

ratio is neglected, as it is really the case for a normal fluid, then the derivative of $(n - n_0)$ with respect to $T$ is given by

$$\left( \frac{\partial n}{\partial T} \right)_p = \left( \frac{\partial n_0}{\partial T} \right)_p + \frac{1}{A_{op}} \left( \frac{\partial n_0}{\partial T} \right)_p \frac{\partial}{\partial T} \left( \frac{\Delta V}{V} \right).$$  (15)

This relation, in view of the coincidence of (11) with (12), is the expression of $(\partial n/\partial T)_p$ deducible from the Onsager theory for the considered system. Since $\Delta V/V$ is defined as the volume fraction occupied by the holes, we have $\Delta V/V = 1 - \varphi$.

4. Interstitial Model

The fundamental hypothesis for an interstitial model is that in a system consisting of $N_1$ molecules part of these, $N_1 f$, lie in the sites of a framework, while the rest, $N_1 (1 - f)$, lie in interstices. The total number of voids is $N_1 f / \nu$, of which $N_1 f / \nu - N_1 (1 - f)$ are unoccupied. The formalism is practically the same for the models proposed in [9] and [10]. We will make use of the formalism...
developed by Mikhailov [9] in his analysis of the Samilov's ice-like model. In such a model, the volume of the system and the volume $V_F$ of the framework coincide while the thermal expansivity of the system is

$$
\frac{1}{V} \frac{\partial V}{\partial T} = \frac{1}{V_F} \frac{\partial V_F}{\partial T} + \frac{1}{f} \frac{\partial f}{\partial T}, \quad (15)
$$

where

$$
\frac{1}{f} \frac{\partial f}{\partial T}
$$

represents the relaxational part of the expansivity and

$$
\frac{1}{V_F} \frac{\partial V_F}{\partial T}
$$
is the lattice expansivity, independent of the occupation degree of the holes and thus coinciding with $A_{0p}$ in (14). Then, assuming the reference state to be that in which all the holes are occupied, $AV/V$ in (13) becomes

$$
\frac{\Delta V}{V} = \left[ 1 - \frac{v}{(v+1)f} \right] = \frac{1}{v+1} \left[ \frac{(f/v) - (1 - f)}{f/v} \right]. \quad (16)
$$

In addition, the employment of the Mikhailov's formalism, after some manipulations, gives

$$
\frac{(f/v) - (1 - f)}{f/v} = \exp \left[ - \frac{v(G_F^0 - G)}{RT} \right]
$$

with

$$
G_F^0 - G = (H_F^0 - H) - T(S_F^0 - S), \quad (17)
$$

where $G$ and $G_F^0$ are the Gibbs molar thermodynamic potentials, respectively, for the system in the present state and for the system in which all the holes are unoccupied.

Substitution of the expression for $\Delta V/V$ given by (16) in (14) yields

$$
\left( \frac{\partial n}{\partial T} \right)_p = \left( \frac{\partial n_0}{\partial T} \right)_p + \frac{1}{A_{0p}} \left( \frac{\partial n_0}{\partial T} \right)_p \frac{1}{v+1} \cdot \frac{\partial}{\partial T} \exp \left[ - \frac{(G_F^0 - G)v}{RT} \right],
$$
or equivalently

$$
\left( \frac{\partial n}{\partial T} \right)_p = \left( \frac{\partial n_0}{\partial T} \right)_p + \frac{1}{A_{0p}} \left( \frac{\partial n_0}{\partial T} \right)_p \frac{1}{v+1} \cdot \frac{1}{v} \frac{\partial f}{\partial T}. \quad (18)
$$

Making use of the value calculated by Mikhailov for $\partial f/\partial T$, we obtain

$$
\left( \frac{\partial n}{\partial T} \right)_p = \left( \frac{\partial n_0}{\partial T} \right)_p + \frac{1}{A_{0p}} \left( \frac{\partial n_0}{\partial T} \right)_p \frac{1}{v+1} \cdot \frac{v(H_F^0 - H)}{RT^2} \exp \left[ - \frac{(G_F^0 - G)v}{RT} \right]. \quad (19)
$$

It is important to note that (19) corresponds to (18) when $(H_F^0 - H)$ and $S_F^0 - S$ are considered constant.

It follows from (19) that $\partial n_0/\partial T$ in the reference state, coincides with the high-temperature limit of $\partial n/\partial T$, which is in agreement with the increase with temperature of the filled holes in all the interstitial models. Therefore, assuming for $\partial n_0/\partial T$ the high-temperature limit, deduced from the best fit of the experimental data,

$$
\partial n_0/\partial T \approx -31.5 \times 10^{-5} \times K^{-1} (H_2O) \approx -32.5 \times 10^{-5} \times K^{-1} (D_2O),
$$

we are able to test this equation. This is feasible only if the entropy and enthalpy differences between the state in which all the holes are unoccupied and the present state, are practically independent of temperature. The test has been performed by rewriting (19) in the form

$$
\ln \left( \frac{\partial n}{\partial T} - \frac{\partial n_0}{\partial T} \right) = \ln \left[ \frac{1}{A_{0p}} \frac{\partial n_0}{\partial T} \frac{v(H_F^0 - H)}{RT^2} \right] + \frac{v(S_F^0 - S)}{R} - \frac{v(H_F^0 - H)}{RT} \quad (19')
$$

and plotting the left-hand side of this equation against $1/T$. The behaviour, as shown by Fig. 2, is linear.

The slope of the water line gives $-1534$ cal/mole for $v(H_F^0 - H)$. Although this result can be compared with the Frank and Quist data [10], we need a few additional steps in our analysis due to the fact that their symbolism is slightly different from
Fig. 2. A test of Eq. (19'): the quantity \(z\), corresponding to the left-hand side of this equation, is plotted against \(1/T\) for water and deuterium oxide.

that introduced by Mikhailov. In the Mikhailov model, the quantity \(H^0_F - H^0_V\) occurs where \(H^0_F\) has the same meaning as in (17) and \(H^0_V\) is the molar enthalpy of the hypothetical liquid comprising molecules lying in the structural holes. In the Frank and Quist symbolism, \(H^0_V\) becomes \(H^0_V = H^0_m + \alpha\) (\(\alpha = \) constant). The numerical value of \(H^0_F - (H^0_m + \alpha)\) is then calculated by fitting the volume vs temperature curve for water. They finally quote the values at \(0\) °C for \(H^0_F - (H^0_m + \alpha)\) and for \(H_L = H\)

\[
H^0_F - (H^0_m + \alpha) = -2210 \text{ cal/mole;}
\]

\[
H = (H^0_m + \alpha) + f[H^0_F - (H^0_m + \alpha)]
\]

\[
= (H^0_m + \alpha) - 1810 \text{ cal/mole}
\]

\(\nu(H^0_F - H)\) can be evaluated from these relations and comes out equal to \(-1532\) cal/mole, in surprising agreement with our value given above.

An analogous computation performed with Mikhailov's data at \(0\) °C \((\nu = 2; f = 0.85; H^0_F - H^0_V = -5000\) cal/mole) leads to the less satisfactory result \(\nu(H^0_F - H) = -1470\) cal/mole. We must consider, however, that this quantity should be variable. No matter how slow one may admit this variation occurs, according to its dependence on \(f\), our results firmly provide evidence that it is constant.

A further control for water may be done by remembering that the thermal expansivity vanishes at \(T = 277.15\) K

\[
\left(\frac{1}{V} \frac{\partial V}{\partial T}\right) = 0.
\]

Therefore, at this temperature, we obtain from (15) and (18):

\[
\left(\frac{\partial n}{\partial T}\right)_{T=277.15} = -\frac{\partial n_0}{\partial T} \left[\frac{\nu}{(\nu + 1)f - 1}\right].
\]

In the Samoilov-Mikhailov model the value \(\nu = 2\) is taken and it is found to be \(f \approx 0.842\) at \(T = 277.15\) K while we get \(f = 0.690\) if we use our data for \((\partial n/\partial T)_p\) and \((\partial n_0/\partial T)_p\). In the Frank-Quist model the different value \(\nu = 3.83\) is chosen and \(f \approx 0.818\) is obtained at \(T = 277.15\) K; this value is in good agreement with the value \(f = 0.821\) we get at the same temperature.

5. Conclusions

It is not to be concluded that our results and the discussion above represent an experimental evidence for the interstitial model examined by Frank and Quist. In spite of a surprising numerical agreement, we must remember that such an agreement is found only at \(0\) °C. At higher temperatures our experimental results clearly show that the temperature dependence of \(\Delta V/V\) occurring in (14) must be different from the theoretical prevision of this model.

Furthermore, it is to be noted that from (16) the quantity

\[
\frac{\Delta V}{V} = \frac{f/v - (1 - f)}{f + f/v}
\]

\[
= \frac{\text{number of unoccupied voids}}{\text{number of sites} + \text{number of voids}}
\]
represents the hole concentration, so that we can only say that the temperature behaviour of $(\partial n/\partial T)_p$ for water and deuterium oxide is consistent with the hypothesis of the existence of holes inside the liquid. It would be easy to show that the same temperature behaviour comes out under the hypothesis of a lattice with a random distribution of non-interacting holes. In this case $\Delta V/V$ is obviously the equilibrium concentration of holes.

In spite of these limitations, however, the numerical agreement found above cannot be considered casual. No comparable results have been obtained in the analysis of other models, e.g. the ice-like model and other models that have not been discussed in this work.

The experimental evidence, therefore, would lead us to state that the Pauling dodecahedral model for water analysed by Frank and Quist involves an essentially correct molecular arrangement even if it is too solid-like to describe really a liquid.

Note that just for that molecular arrangement this model finds a justification in the more general and reasonable “random network model” [11] [12].

Finally, it results implicitly from

$$\varphi = 1 - (\Delta V/V)$$

or, equivalently, from (16)

$$\varphi = \frac{V}{V_F} = \frac{1}{V} \cdot \left(1 - \frac{1}{f} \right)$$

($V_F$, temperature dependent)

that, except in the reference state, we never used for $\varphi$ the Onsager statement nor the Böttcher one. Therefore, in view of the previous hypothesis about the inadequacy of the O-B relation, it seems reasonable to fit, at least in this case, the experimental data owing to the assumptions on $\varphi$.