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Abstract

Full Text

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MEASUREMENT OF THE REFRACTIVE INDEX OF STRUCTURALLY MODIFIED WATER BY A CAPILLARY MICROMETHOD

Structurally modified water, formed under a dynamic regime of vapor condensation on the surfaces of glass and quartz, differs sharply in its physical properties from ordinary water ($^{1-4}$). This liquid is a two-component system consisting of molecules of ordinary water and an anomalous component (^{4,5}). It has been suggested that the latter is represented by stable polymeric molecules of water $(H_2O)_n$ ($^{4-6}$). The considerable increase in the density of the modified water, to 1.35-1.4 g/cm^3 (^{5}), gave grounds to suppose that differences in its refractive index would be just as noticeable.

Structurally modified water is usually obtained in capillaries with diameters d = 10-50 μ in amounts of 10^{-5}-10^{-7} g. In view of this, for measuring the refractive index, on the suggestion of I. V. Obreimov, a capillary micromethod was used. The idea of this method is that the liquid filling the capillary channel forms a cylindrical lens, whose refractive index can be determined from its focal length. In order to exclude refraction of light by the body of the capillary, the latter is placed in an immersion liquid having the same refractive index as quartz (CCl_4 or a solution of water in glycerin).

Fig. 1. Diagram of the apparatus for measuring the refractive index of liquids in thin capillaries

The layout of the apparatus for measurements of the refractive index n is shown in Fig. 1. A quartz capillary 1 with a column of modified water is illuminated by a parallel beam of rays traveling along the axis of an MIN-8 microscope. In the microscope 2, the image of the light source was observed (and photographed),

Fig. 2

Figure 2: Fig. 2

formed by the rays after their refraction by the liquid filling the capillary channel. The white-light source 4 built into the microscope, with a system of lenses 5, was used to create a parallel beam of rays. The capillary on a support was placed in a thermostatted cuvette 3 with immersion liquid 6.

It is easy to show that the paraxial beam must be focused at a distance f from the capillary axis:

$$f = \frac{nd}{(n - n_k)4}, \tag{1}$$

where n and n_k are, respectively, the refractive indices of the liquid under investigation

bone and quartz. For $n < n_k$ the liquid in the capillary forms a diverging lens, and for $n > n_k$, a converging one. In the first case the rays are focused below, and in the second—above the axis of the capillary (Fig. 1).

Since in narrow capillaries it was difficult to restrict the light beam, strong spherical aberration was always present.* The microscope was focused on the plane that corresponded to the greatest sharpness of the image of the light source—the scattering band. It is difficult to calculate the position of this plane, since it is determined by the shape of the caustic and by the distribution of energy in the scattering band (7).

Fig. 2. Dependences of $\Delta f/d$ on n, obtained experimentally in a quartz capillary with $d = 23\,\mu$ (**curve 1**) and calculated from equation (2) (**curves 2**).

For these reasons, in order to determine the refractive index it was more reliable to use calibration graphs obtained experimentally. For this purpose, the same quartz capillary was filled with reference liquids having different refractive indices ($n = 1.334$-1.66). However, the position of the axis of the capillary channel, from which the focal distance had to be measured, could not be determined with sufficient accuracy. Therefore the measurements were made not of the focal distance itself, but of the difference between the focal distances for the empty (f_0) and liquid-filled (f) channel of the same capillary,

$$\Delta f = f_0 - f = n_k d(n - 1)/(n_k - 1)(n - n_k)4 \tag{2}$$

Figure 2 shows the experimentally obtained calibration dependences of $\Delta f/d$ on n for various liquids (curve 1). Curves 2 were constructed from equation (2). For the reasons indicated, exact agreement between the experimental and theoretical data could not be expected. The similar character of these dependences confirms the correctness of the basic concepts of the theory of the method.

From equation (2) and similarity considerations it is clear that the ratio $\Delta f/d$ should not depend on the capillary diameter. This was confirmed by direct experiments with columns of water ($n = 1.334$) and amyl alcohol ($n = 1.41$) in quartz capillaries. For $d > 10\,\mu$, the ratio $\Delta f/d$ remains constant, and the dependences of $\Delta f/d$ on n pass through the origin.

For calculations of the refractive index of modified water, the calibration graphs of Fig. 2 were used. The capillary diameter was determined (after the Δf measurements had been carried out) in the end section by means of a microscope with an ocular micrometer. The cuvette with the sealed capillary was placed on the microscope stage in such a position that the liquid column occupied 2/3 of the field of view. The distance Δf between the images produced by the empty and liquid-filled channel of the capillary was determined from the scale of the microscope micrometer screw with an accuracy of $\pm 1\,\mu$. Objectives 40×0.30 were used (when the image of the source was far below the capillary axis), as well as 60×0.85 and 90×1.25. For photography, a photomicrographic attachment with a 15× eyepiece was used. The refractive index was determined from the value of Δf, obtained as the arithmetic mean of 8-10 measurements. For capillaries $d > 10\,\mu$, the accuracy of determining n by this method is estimated by an error of the order—

* Except for the empty channel, when the beam is limited because of total internal reflection of the peripheral rays.

$\cdots \pm 0.005$. For capillaries of smaller diameters the error increases because of the reduced accuracy of measuring both d and Δf.

Figure 3 shows, by way of example, a microphotograph of columns of ordinary (1) and maximally modified water (2) brought into contact. The microscope is focused on the center of the capillary channel, as follows from the sharp diffraction pattern on the walls and on the menisci. The presence of an interphase boundary indicates a surface tension at the interface between ordinary and maximally modified water that is different from zero.

Fig. 3. Microphotograph of columns of ordinary (1) and maximally modified (2) water in a quartz capillary, $d = 15.5\,\mu$

However, after several days, as a result of mutual diffusion of the components, the interphase boundary disappears—complete dissolution occurs. The course of this process could be followed by monitoring the change in the refractive index of the columns. At the beginning of the observations, for the left-hand column $n = 1.334$, and for the right-hand column $n = 1.482$. Subsequently the values of n for the left-hand column increased, while for the right-hand column they decreased. Upon complete mixing, the same value of n was established throughout the entire volume of the liquid.

Measurements carried out for various columns of modified water showed that the values of their refractive indices lie in the range from $n = 1.335$ for very weakly modified water to $n = 1.48$–1.5 for maximally modified water.

For frequencies corresponding to light oscillations, the contribution of the permanent dipole moment of water molecules is insignificant. In this case, according to the Lorentz-Lorenz equation, the magnitude of the refractive index n depends only on the quasielastic polarizability β of the electron shell of the molecules:

$$(n^2 - 1)/(n^2 + 2) = {}^4/_3 \pi N \beta. \tag{3}$$

Here $N = \rho N_a / \mu$ is the number of molecules per unit volume, which can be expressed through the density of the dielectric ρ, its molecular weight μ, and Avogadro' s number N_a.

It is known that for water the molecular refraction $R = \mu(n^2 - 1) : \rho(n^2 + 2)$ depends only weakly on its aggregate state ([8], [9]). Thus, for water vapor $R = 3.7$ cm^3, for liquid water $R = 3.71$ cm^3, and for ice $R = 3.78$ cm^3. Thus, intermolecular interaction has practically no effect on the polarizability of water molecules. This gives grounds to suppose that it also does not change in the presumably polymeric molecules of the anomalous component. Then N should still remain the number of monomeric water molecules and, consequently, in calculations of R one should use the value $\mu = 18$. Taking $\rho = 1.4$ g/cm^3 and $n = 1.49$ for maximally modified water, we obtain $R = 3.7$ cm^3, which coincides with the known value of molecular refraction for ordinary water.

This result confirms that the maximally modified water consists of H_2O molecules packed more densely than in ordinary water and contains no (at least in appreciable amounts) other atoms or molecules with a different polarizability.

In conclusion, it should be noted that the micromethod developed makes it possible to estimate rapidly the density of modified water and to characterize the content of the anomalous component in it. These measurements can be carried out on very short columns only 10–20 μ in length, which cannot be done by other methods. Thus, for example, reliable control of the degree of modification in the course of thermal expansion is possible only for columns more than 2–3 mm long ([3]). In addition, the use of this method makes it possible to determine local values of n, which permits observation, for example, of the diffusion processes of the anomalous component in the volume of columns of modified water.

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