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Abstract

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PHYSICS

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MEASUREMENT OF THE DENSITY OF DROPLETS

OF STRUCTURALLY MODIFIED WATER

The structurally modified state of water differs sharply from ordinary water in its lowered vapor pressure (^{1,2}), increased viscosity (^{2,3}), and different course of thermal expansion (^{4,5}). Modified water behaves as a system consisting of two components with limited mutual solubility (^{5,6}). It was natural to expect that the change in the properties of water should also manifest itself in a change in its density. In particular, the supposition was expressed that the density of structurally modified water is increased (^{1}).

Since the quantities of anomalous water obtained are small (10^{-4}—10^{-6} g), measurement of its density by a weighing method could not be carried out with the necessary accuracy. It was therefore decided to use the method of hydrostatic weighing (^{7}). A glass column 1.5 cm in diameter and 20 cm high was filled to half its height with tetrabromoethane (density $\rho = 1.619$ g/cm^3) or carbon tetrachloride ($\rho = 1.595$ g/cm^3), and then with vaseline oil ($\rho = 0.87$ g/cm^3). After prolonged standing in a desiccator (20–40 days), as a result of mutual diffusion, an almost linear distribution of the density of the liquid* was established in the column over the interval $\rho = 1 \div 1.4$ g/cm^3. Calibration was carried out with the aid of reference droplets and particles 1–3 mm in size with known density (drops of water and of aqueous solutions, particles of polystyrene and plexiglass).

Columns of modified water were obtained by the ampoule method (^{8}) in quartz capillaries 30–50 μ in diameter. In a number of cases, portions of modified water were preliminarily enlarged by distillation from several narrow capillaries into one wider capillary.

The modified water was forced into the column by a piston syringe, to the needle of which the end of the capillary was attached through a rubber stopper. The

Fig. 1

Figure 1: Fig. 1

detachment of droplets, which occurred upon a sharp push of the capillary, was monitored microscopically. The diameters d of the sedimenting drops of water were usually from 100 to 300 μ. The positions of the reference objects and droplets were recorded with the aid of a microscope (with an accuracy of ± 0.1 mm) mounted on a universal stand. To illuminate the column when taking readings, OI-19 illuminators with a heat filter were used. The vertical density gradients formed in the columns were $\sim 5 \cdot 10^{-2}$ g/cm^4. This made it possible, taking into account the capabilities of the measuring instruments, as well as the investigated local disturbances of the density field in the volume of the liquid**, to determine the density of droplets with an accuracy on the order of 0.1%.

However, owing to the small but finite (less than 0.01%) solubility of water in the liquids filling the column, the sizes of small droplets of ordinary water, as was found, decreased during the experiment. For the same reason, droplets of two-component systems—modified— of water and salt solutions—after approaching the mark corresponding to their density, subsequently did not come completely to rest, but, having sharply reduced their speed, continued to settle. This made it impossible to determine the density of the drops from their equilibrium position in the column (which was reached only after 2-3 days) and forced us to turn to an analysis of the sedimentation-velocity graphs. The sedimentation velocities were determined from the time taken by the drops to pass a definite section of the microscope scale. In Figs. 1 and 2 the dependences obtained are shown for the sedimentation velocities of drops on their distance H from the liquid level in the column (curves 2 and 3). The distribution of the liquid density ρ along the height of the column is shown by curves 1 in the left-hand part of the figures. The passage of the falling-velocity curves through a maximum is associated with a change in the viscosity of the liquid, which decreases from $\eta \sim 100$ cP in the upper part of the column (vaseline oil) to $\eta \sim 1$ cP in the lower part (carbon tetrachloride).

Fig. 1. Distribution of density ρ over the height H of the column (1) and graphs of the falling velocities v of drops of an aqueous solution of $MgCl_2$ with density 1.11 g/cm^3 (2—a drop of diameter $d \sim 300$ μ; 3—$d \sim 70$ μ).

The sedimentation graphs for drops of an aqueous $MgCl_2$ solution with known density ($\rho = 1.11$ g/cm^3), checked pycnometrically, are shown in Fig. 1. Let us estimate the density of these drops by extrapolating the linear portions of

* It was possible to shorten the waiting time by applying carefully dosed stirring in the middle third of the mixture column.

** Investigated by comparing the levels at which reference droplets and particles introduced at different distances from the axis of the column came to rest.

Fig. 2

Figure 2: Fig. 2

Figure 3

Figure 3: Figure 3

the graphs $v(H)$ to zero velocity (dashed lines). As is seen from the graphs, for large drops of the solution ($d \sim 300\ \mu$) the density values obtained in this way practically coincide with the actual ones. For small drops ($d \sim 70\ \mu$) the density measured by this method proves to be somewhat overestimated ($\rho = 1.12$ g/cm^3). However, the discrepancy in the ρ values did not exceed 0.01 g/cm^3.

Experiments show that the falling velocities of the drops decrease sharply when they reach a layer of the column with a density close to the density of the liquid in the drop. The time elapsed from the beginning of sedimentation to the sharp slowing was $\tau_0 = 15$ min for a large $MgCl_2$ drop and $\tau_0 = 2$ h for $d \sim 70\ \mu$. The further slow sedimentation of the drops, observed over 2–3 days, was caused by the slowly proceeding extraction of water from them by the liquid filling the column. This is also confirmed by direct microscopic measurements of the drop diameters. Thus, for example, the sizes of drops of $MgCl_2$ solution ($d \sim 200\ \mu$) decreased by approximately a factor of 1.5 over 2 days. The larger the ratio of the surface of a drop to its volume, i.e., the larger the drop, the less pronounced is the influence of dissolution. Expe-

Fig. 2. Distribution of density ρ over the height H of the column (1) and graphs of the falling velocities v of drops of structurally modified water (2—a drop of diameter $d \sim 150\ \mu$; 3—$d \sim 100\ \mu$).

experiments carried out with salt solutions show that the possible error of density measurement in the gradient column for drops with $d \geq 100\,\mu$ does not exceed 1% for $\tau_0 \leq 1$ h. For drops of smaller size the measurement error increases.

Figure 2 shows plots of the falling velocities of drops of structurally modified water with diameter $d \sim 150\,\mu$ (2) and $d \sim 100\,\mu$ (3). In this case an analogous picture is observed, of two successive stages of sedimentation—fast and slow. The second stage, obviously, is due to extraction by the column liquid of the "normal" component of the water, while the other component, which is considerably less volatile, remains. Extrapolation to $v = 0$ of the linear portions of the plots $v(H)$ (dashed lines) gives density values of the modified water equal, respectively, to $\rho = 1.15$ g/cm^3 and $\rho = 1.21$ g/cm^3. Since τ_e was approximately 30 min, the effect of extraction could not have been significant.

Fig. 3. Relative temperature changes in the length $\Delta l/l_0$ of columns of structurally modified water (l_0 is the length at $t = 0$°C), whose density was then

determined in a gradient tube.
1—l_0 = 9.5 mm; $\rho = 1.27$ g/cm^3; 2—l_0 = 5.3 mm; $\rho = 1.21$ g/cm^3; 3—l_0 = 13.5 mm; $\rho = 1.15$ g/cm^3; 4—l_0 = 28 mm; $\rho = 1.01$ g/cm^3; 5—ordinary water; $\rho = 1$ g/cm^3; 6—maximally modified water (^{6}), $\rho = 1.35$-1.4 g/cm^3.

The density values obtained refer to water of an intermediate degree of anomalousness, as follows from analysis of the thermal-expansion plots shown in Fig. 3. Measurements of the course of thermal expansion were performed by the method (^{4,5}) for columns of anomalous water in quartz capillaries before it was pressed out into the column. In Fig. 3, curve 2 corresponds to anomalous water with density $\rho = 1.21$ g/cm^3, and curve 3 to a drop with density $\rho = 1.15$ g/cm^3. The same graph also shows the course of thermal expansion for anomalous water with density $\rho = 1.27$ g/cm^3* (curve 1) and $\rho = 1.01$ g/cm^3** (curve 4), measured by the same method. Dashed lines 5 and 6 characterize the course of thermal expansion, respectively, of ordinary water (tabulated values) and of maximally modified water (^{6}). Comparison of curves 1-4 with these two limiting cases makes it possible to estimate the degree of anomalousness of the structurally modified water whose density was measured.

As is seen from Fig. 3, an increase in the content of the anomalous component leads to an increase in the density of structurally modified water. The density values measured for drops differing in the degree of "anomalousness" lay in the range from 1.01 to 1.3 g/cm^3. Columns of modified water grown in evacuated chambers (^{2,4}) or ampoules (^{8}) at $p/p_s = 0.95$-0.97 usually have a density $\rho =$ 1.1-1.2 g/cm^3, considerably exceeding the density of normal water. The density of modified water decreases when it is diluted, for example, by condensation of ordinary-water vapor on the column. Conversely, evaporation of structurally modified water leads to an increase in its density due to the concentration of the less volatile anomalous component.

As a result of extraction of the normal component in the column, droplets of modified water, as is seen from Fig. 2, after sharp braking settle with a sharply reduced velocity, very slowly decreasing in size. After several days (if no sticking to the wall of the column occurred) the droplets stopped at the mark corresponding to a liquid density $\rho = 1.35$–1.4 g/cm^3 (see, for example, Fig. 2, curve 2). These values can apparently serve as an estimate of the density of the maximally modified water, which, like ordinary water, is a one-component system (^{6}). Since maximally anomalous water is difficult to squeeze out of a capillary because of its high viscosity, it has not yet been possible to measure its density directly by the hydrostatic method.

As was shown earlier (^{5}), the density of droplets of the α-phase of modified water in the region of phase separation is higher than that of the β-phase. This

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* The drops pressed out into the column had sizes $d \sim 200\,\mu$ and $d \sim 300\,\mu$.
** Drop diameter $d \sim 100\,\mu$.

now makes it possible to conclude that the α-phase differs by a higher content of the anomalous component. It is a solution of ordinary water in maximally modified water, whereas the β-phase is a solution of the anomalous component in ordinary water. The temperature at which droplets of the β-phase disappear (^{5}) corresponds to the upper mixing temperature of these two liquids.

Phase separation of the system upon freezing makes possible an estimate of the weight content of the anomalous component $c = m_a/m$, where m_a is the mass of the anomalous component and m is the mass of the entire column. As is known, at low temperatures the mutual solubility decreases sharply. Therefore, as a first approximation one may (at sufficiently low temperature) neglect, in approximate calculations, the content of the anomalous component in the solidified β-phase (and take its density as equal to that of ordinary ice, ρ_l) and neglect the presence of normal water molecules in the vitrified α-phase, taking its density as $\rho_a =$ 1.35–1.4 g/cm^3. Then $c = 1 - \rho_l(\rho_a - \rho_t)/\rho_t(\rho_a - \rho_l)$, where ρ_t is the density of the column of modified water after solidification.

For modified water with density $\rho = 1.21$ g/cm^3 (Fig. 3, curve 2) the jump in volume upon solidification is about 7%, which leads to values $\rho_t = 1.13$ g/cm^3. Substituting this value of ρ_t into expression (1), we obtain $c \sim 0.56$. From this one can find the volume fraction of the β-phase in the solidified column of anomalous water, $v_\beta = \rho_t(1 - c)/\rho_l$.

Carrying out the calculations, we obtain $v_\beta = 0.54$. This is close to the earlier estimate (^{5}), made by an independent method, of v_β for water of approximately the same degree of anomaly. The latter is confirmed by the closeness of the thermal expansion curves obtained in work (^{5}) and presented in Fig. 3 (curve 2).

The results of the work lead to the conclusion that the density and, consequently, the structure of modified water are strongly altered under the influence of the presence of molecules of the anomalous component. This explains the sharp and therefore easily observable differences between its properties and those of ordinary water, discovered in earlier experiments ($^{1-6}$).

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