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Abstract

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FINE STRUCTURE OF RAYLEIGH LIGHT SCATTERING IN SOLUTIONS AND DISPERSION OF HYPERACOUSTIC OSCILLATIONS

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Rayleigh scattering of light in solutions is caused by adiabatic and isobaric density fluctuations, orientation fluctuations, and concentration fluctuations. In order experimentally to separate the total scattering of light into its component parts, determined by different kinds of fluctuations, it is necessary to investigate the fine structure of Rayleigh scattering. Such an investigation in many cases also makes it possible to find the propagation velocity of hyperacoustic oscillations. The fine structure of light scattered by individual liquids has been studied by a number of authors (^1). For solutions, up to now only two attempts at qualitative measurements are known, which did not lead to any definite conclusions (^2,3). The hyperacoustic properties of solutions have not been studied up to the present time.

The apparatus we constructed for photographing the fine structure of the Rayleigh line of scattered light is, in the main, analogous to the apparatus described in (^1). The resolving power of the Fabry–Perot interferometer in our experiments was 800,000. The cuvette with the liquid under study was thermostated with an accuracy of $±$0.5°. We studied acetone–water and methyl alcohol–water solutions at 25° and at concentrations, in mole fractions, of acetone: 0.0; 0.06; 0.2; 0.4; 0.7; 1.0 and of methyl alcohol: 0.15; 0.36; 0.6; 1.0. For each concentration the measurements were made 5 or more times. In each of the photographs, 3–4 neighboring interference orders were taken into account. Thus the measurement results given below are mean values from 15–20 or more determinations of the elements of the fine structure. The measurements were made on the line λ4358 Å of the mercury spectrum. In addition, for water, parallel measurements were carried out on the line λ4046 Å. The photographs were photometered on an MF-4 microphotometer and interpreted by the method described in (^1), in several parallel variants. The very small parasitic scattering was controlled by photographs of the fine structure of water (by the absence of an unshifted component). A series of photographs was obtained at an interferometer resolving power equal to 1,200,000. In individual cases the exposure time reached 3 days.

Figure 1 gives the curves of the propagation velocity of hyperacoustic oscillations

Figure 1: Dependence of the velocity of ultraacoustic vibrations (a) and the velocity of hyperacoustic vibrations (b) on concentration for the acetone–water system and for the methyl alcohol–water system.

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Figure 2: Dependence of the refractive index n_λ (1) and of the ratio of the intensity of the central component to the sum of the intensities of the shifted components $I_c/2I_{cm}$ (2) on concentration for the acetone–water system and for the methyl alcohol–water system.

Figure 2: Figure 2: Dependence of the refractive index n_λ (1) and of the ratio of the intensity of the central component to the sum of the intensities of the shifted components $I_c/2I_{cm}$ (2) on concentration for the acetone–water system and for the methyl alcohol–water system.

in acetone–water solutions ($\omega \approx 0.6 \cdot 10^{10}$ sec^{-1}, $\Lambda \approx 22 \cdot 10^{-6}$ cm) and methyl alcohol–water ($\omega \approx 0.5 \cdot 10^{10}$ sec^{-1}; $\Lambda \approx 22.0 \cdot 10^{-6}$ cm), calculated from the formula

$$\frac{\Delta\nu}{\nu} = 2n\frac{v}{c}\sin\frac{\theta}{2}.$$

For comparison, data ([4,5]) are given on the propagation velocity of ultrasonic oscillations ($\omega \approx 56 \cdot 10^5$ sec^{-1}, $\Lambda \approx 24 \cdot 10^3$ cm). In water and in the solutions a considerable **negative** dispersion of hyperacoustic oscillations is observed, with $\Delta v/v$ reaching $\sim 5\%$, whereas the root-mean-square error in the determination of v is $\sim 1.4\%$. With decreasing water concentration x_1, the negative dispersion of hyperacoustic oscillations gradually disappears; moreover, in the acetone–water system the disappearance of the dispersion is obser–

is attained at $x_1 = 0.65$, and in the methyl alcohol–water system at $x_1 = 0.5$. In more concentrated solutions of acetone and methyl alcohol, no dispersion of hypersonic waves is observed. As is known, up to the present time negative dispersion of acoustic vibrations in individual

Fig. 1. Dependence of the velocity of ultraacoustic vibrations (a) and the velocity of hyperacoustic vibrations (b) on concentration for the acetone–water system and for the methyl alcohol–water system

liquids and solutions has not been observed. The data available in the literature on the existence of negative sound dispersion in carbon disulfide, acetone, and some other liquids have not been confirmed (see ([6]), pp. 271–272).

Fig. 2. Dependence of the refractive index n_λ (1) and of the ratio of the intensity of the central component to the sum of the intensities of the shifted components

$I_c/2I_{cm}$ (2) on concentration for the acetone–water system and for the methyl alcohol–water system

The negative dispersion of hypersonic waves that we have found in water and aqueous solutions is apparently due to the structural relaxation of water. The anomalous character of the dispersion agrees with the known anomalous properties of water and can be explained on the basis of existing theoretical ideas about the nature of sound dispersion.

We then compared the integrated intensities of the central component I_c and of the Mandelstam-Brillouin components I_{cm}. Figure 2 presents curves showing the dependence of the ratio $I_c/2I_{cm}$ on the composition of the solution. To analyze these curves it is necessary to take into account the dependence of the refractive index n_λ on concentration. The graphs $n_\lambda = f(x)$ are also shown in Fig. 2.

In solutions, the central component of the Rayleigh triplet is caused not only by isobaric density fluctuations, but also by concentration fluctuations; moreover, the intensity of scattering by concentration fluctuations is

$$I_k \sim \left(\frac{\partial n}{\partial x}\right)^2 \overline{(\Delta x)^2}.$$

In acetone-water solutions there are large positive deviations from Raoult' s law and, consequently, the concentration fluctuations are large; they reach their greatest value at $x_1 \simeq 0.4$. It is precisely in this concentration interval that n_λ passes through a maximum, $\partial n_\lambda/\partial x \simeq 0$, and, consequently, concentration scattering is practically absent. Therefore $I_c/2I_{cm}$ in this concentration region passes through a minimum. It is interesting to note that in this concentration region $I_c \simeq I_{cm}$.

Methyl alcohol-water solutions are close to ideal; the concentration fluctuations are very small and do not make a noticeable contribution to Rayleigh light scattering. Therefore the dependence of $I_c/2I_{cm}$ on concentration in this case has a different form. We note that $I_c/2I_{cm}$ passes through a maximum, and the maximum of the ratio $I_c/2I_{cm}$, as Fig. 2 shows, occurs in the same concentration region as the maximum of the refractive index. At the maximum $I_c \simeq I_{cm}$. The accuracy in determining I_c and I_{cm} is about $\pm 10\%$.

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Note: Figure translations are in progress. See original paper for figures.