

KINETICS OF CONCENTRATION FLUCTUATIONS IN ISOCTANE-NITROETHANE SOLUTIONS HAVING A CRITICAL STRATIFICATION POINT

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Information on the kinetics of concentration fluctuations can be obtained from acoustic measurements. To this end, we investigated the absorption coefficient α and the sound propagation velocity V in nitroethane-isooctane solutions. This system has a critical stratification point $x_c \approx 0.4$ (x - molar fraction of the isooctane). The refractive indices of the solution components differ by only 0.0005 at 20°. An exact determination of the temperature at which the meniscus vanishes is therefore difficult. Measurements made by M. A. Anisimov in our laboratory have shown that $T_c = 31.0 - 31.5^\circ\text{C}$. Ultrasonic measurements of α were made in the frequency interval 24 - 950 MHz. The solution was kept at constant temperature within $\pm 0.05^\circ$. The ultrasound velocity was measured at 24 - 100 MHz. The measurement procedure is described in [1]. Hypersonic measurements of α and V were made with the aid of a helium-neon laser and were published earlier [2]. No acoustic dispersion was observed in pure nitroethane up to frequencies $\sim 4 \times 10^9$ Hz. A decrease of α/f^2 from 62×10^{-17} to 49×10^{-17} sec²/cm, and a slight increase of V were observed in isooctane at $f > 1 \times 10^9$ Hz. The acoustic dispersion in the isooctane is due to the rotational-isomeric transformations of its molecules. In the nitroethane-isooctane solutions, α/f^2 increases sharply, passing through a maximum at $x = x_c$ (see Fig. 1). This gives rise to a new region of acoustic dispersion in the solution, connected with the presence of concentration fluctuations. A detailed description and an analysis of the measurement results will be presented later. We note here the following singularities of this region of sound dispersion.

1. The new region of dispersion of α/f^2 and the associated increase in sound absorption are observed at ultrasonic frequencies. At hypersonic frequencies $f \approx 3 \times 10^9$ Hz, the value of α/f^2 not only fails to increase when $x \approx x_c$, but even has a certain tendency to exhibit a minimum (see [2] and Fig. 1).

2. At all concentrations and in the entire frequency interval under investigation, the dependence of the sound absorption on the frequency $\omega = 2\pi f$ is given by a power-law function (see Fig. 2):

$$a' = a \omega^{p+1}; \quad (1)$$

$$\frac{a'}{f^2} = \frac{a}{f^2} - B, \quad (2)$$

where B , a , and p are empirical constants. The power exponent lies in the interval

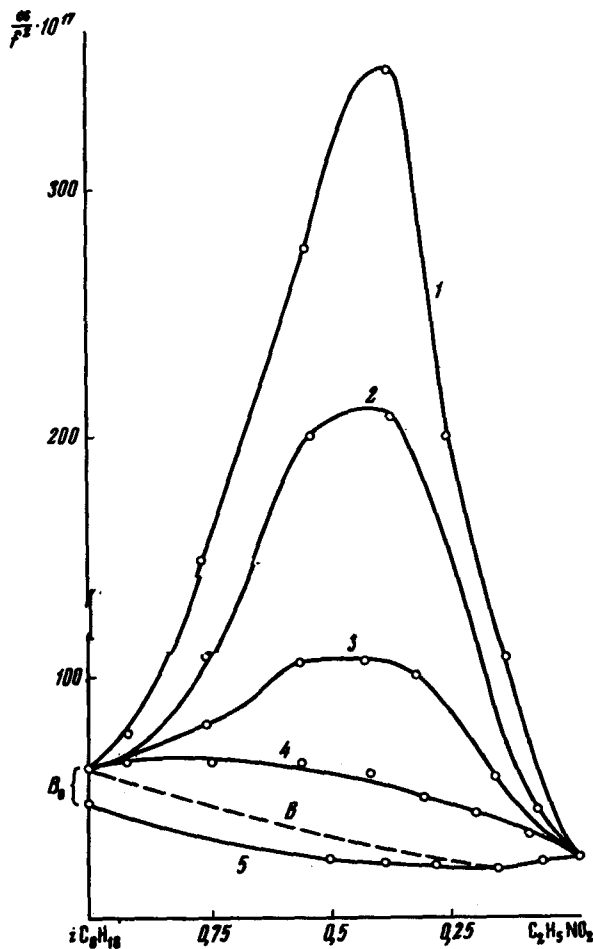


Fig. 1. Dependence of α'/f^2 on the isooctane concentration x at different frequencies: 1 - 24 MHz, 2 - 40 MHz, 3 - 136 MHz, 4 - 950 MHz, 5 - 3500 MHz. Dashed - the parameter B (see Eq. (2)).

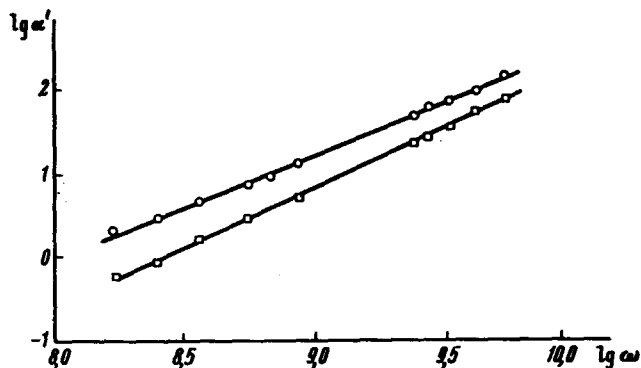


Fig. 2. Plot of $\log \alpha'$ vs. $\log \omega$:
 O) $x = 0.404$, $p = 0.21$, $B = 39 \times 10^{-17} \text{ sec}^2/\text{cm}$;
 □) $x = 0.197$, $p = 0.46$, $B = 33 \times 10^{-17} \text{ sec}^2/\text{cm}$.

$0 < p < 1$. When $x \rightarrow x_c$ and $T \rightarrow T_c$, the exponent decreases and the coefficient a increases.

3. The dispersion of α'/f^2 is not accompanied by appreciable changes in the sound velocity V . The observed changes of V do not exceed $\sim 1 - 2\%$. To describe the frequency dependence of the sound absorption coefficient it is necessary to introduce the relaxation-time

spectrum. Knowing the density of the relaxation-time spectrum, it is possible to calculate the average relaxation time τ_α , which characterizes the average lifetime of the Fourier components of the concentration fluctuations. It turns out here that τ_α increases sharply in the vicinity of the critical point and retains rather large values in a fairly wide interval of concentrations and temperatures. This can be used to explain the attenuation of the diffusion in the vicinity of the critical point [3,4].

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CATHODOLUMINESCENCE OF SOLID XENON IN THE ULTRAVIOLET REGION OF THE SPECTRUM

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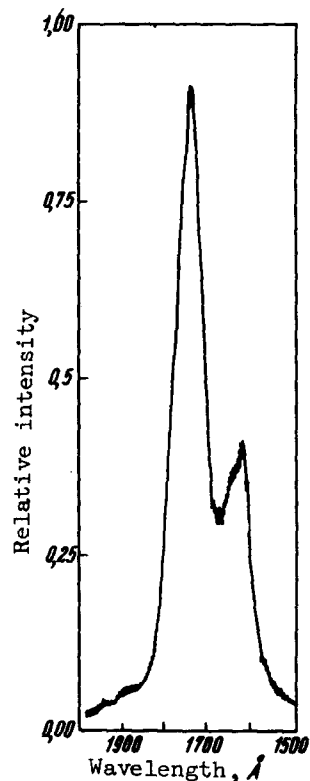
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In view of the fact that the effective temperature of an electron beam used as a laser-pump source is very high, this method can be used to excite practically all energy levels. We observed the luminescence of solid xenon grown from the gas phase and bombarded with fast electrons. The luminescence spectrum (see the figure) consists of two lines. 1735 and 1620 Å. The width of the more intense line is ~ 70 Å and the distance between lines is ~ 115 Å. The spectra were recorded with a vacuum spectrometer with a diffraction grating; the spectrum shown in the figure was recorded at a spectrometer resolution ~ 2.5 Å. The electron energy was 300 - 400 keV, the electron-current pulse duration was 50 nsec, and the pulse repetition frequency was 10 Hz. The initial xenon was $\sim 99.5\%$ pure. The crystal temperature was maintained within the range 60 - 70°K. The total power of one emission pulse reached several hundred watts.

The observed luminescence is apparently connected with the emission of localized excitons. The Stokes shift of the emission line is 2 eV. A Stokes shift of like magnitude was observed in [1], where measurements were made of the luminescence spectra of solid xenon excited by α particles from a radioactive source (5 mCi and Po²¹⁰). The luminescence spectrum in the cited investigation consisted of one line near 1730 Å of width $\sim 100 - 120$ Å. The excitation intensity was much lower in [1] than in our inves-



Luminescence spectrum of solid xenon subject to electron excitation.