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DETERMINATION OF CHANGES IN INTERMOLECULAR "FREE VOLUME" OF LIQUIDS AT DIFFERENT PRESSURES FROM HYPERACOUSTIC DATA

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Abstract

A great contribution to the study of the liquid state can be made by finding out the nature of the change in the intermolecular space (free volume) between liquid molecules at various state parameters. Optical methods will give us the opportunity to obtain more complete information about the nature of the change in the free volume between the molecules of liquids. One of these methods is based on the study of the Mandelstam-Brillouin light scattering spectra. In the work, the velocities of hypersonic propagation along the Mandelstam-Brilyuin spectra of light scattering were investigated, and on the basis of the hypersonic velocity, the volume of micro voids (free volume) between liquid molecules was calculated.

As can be seen from the results obtained, with an increase in pressure and molecular weight of alcohols, the volume of micro voids between the liquid molecules decreases. This is fully consistent with the main provisions of the hole theory of J.I. Frenkel.

Keywords; Liquid, alcohols, pressures, microvoids, "hole theory", free volume, hypersound, light scattering.

Introduction

The development of the molecular theory of liquid states of matter contributes to the solution of applied problems in many branches of science and technology. However, the molecular theory of the liquid state of matter lags far behind in its development from that of gases and solids.

In model theory, they played a huge role in understanding the structure and nature of the liquid state of matter. These theories are based on the concept of free volume of liquid. This concept was first introduced by van der Waals and is considered as a volume not occupied by molecules in a liquid. Later, the concept of free volume was developed in the works of J.I. Frenkel, Eyring /1-2/, and they are widely used in modern research when interpreting experimental results.

According to the cell theory /1, 3/ the additional volume that the substance receives at the pressure of the crystal is evenly distributed among the cells.

According to the hole theory of J.I. Frenkel /1/, the main factor determining the structure of liquids is the free volume. The excess volume, usually called the "free volume" of the liquid, creates the "space" that ensures the individual mobility of the liquid particles and thereby its fluidity. The theory assumes that all the difference between a liquid and a crystal is due to the presence in the lattice of a significant number of unfilled nodes, i.e. "holes".

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According to the hole theory of the dependence of hypersound velocity on pressure, it has the following form:

$$(1)\vartheta = \vartheta o \exp(\frac{P*Vh}{2kT})$$

If we determine the "free volume" from this equation, i.e. the volume of micro voids, we have the following formula:

$$V_h = Ln \qquad (2)\frac{\vartheta}{\vartheta}\,\frac{2kT}{P}$$

Where, V_h is the volume of micro voids between the molecules of liquids (free volume), is the hypersonic velocity under normal conditions, is the hypersonic velocity at different pressures, k is the Boltzmann constant, T is the absolute temperature, P is the pressure created by the high-pressure cell.$\vartheta o \vartheta$

To solve the problem, a spectral apparatus assembled on the basis of a Fabry-Pierrot interferometer with a dispersion region of 0.625 cm2 was used. The excitation light source was a helium-neon laser with wavelength = 6328 Aλº /4/.

Pressure studies were carried out in a special high-pressure cell. The high-pressure cell is a cylinder with a working volume of 30 cm3 and is made of the most stainless steel. The principle of creating pressure in it is that in a high-pressure chamber, inside the liquid under study, there is a metal bellows, the surface of which is chrome-plated. Oil is pumped into the bellows with the help of UNGR 2000 through a high-pressure steel capillary, while the bellows expands and creates pressure in the liquid. The pressure value inside the chamber is controlled by a liquid pressure gauge. The chamber has four mutually perpendicular windows made of quartz. Mandelstam-Brillouin scattering spectra are taken at an angle of 900 from the side windows.

Taking into account the tasks set, we studied the Madelstamm-Brillouin spectra of light scattering in a number of normal alcohols and calculated the speed of hypersonic propagation according to formula (3):

$$\vartheta_{\text{гз}} = \frac{\Delta\nu \cdot c \cdot \lambda}{2 \cdot n \cdot sin\frac{\theta}{2}} \quad (3)$$

Where, is the displacement of the Mandelstamm-Brillouin component, c is the speed of light, is the wavelength of laser radiation, n is the refractive index of the liquid under study, and is the scattering angle. $\Delta\nu$ λ θ

We have studied the velocities of hypersonic propagation along the Mandelstam-Briluenovsky spectra of light scattering, a number of normal alcohols, and on the basis of the hypersonic velocity, we have calculated the volume of micro voids (free volume) between the molecules of a number of normal alcohols at different pressures.

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The results obtained are shown in Table 1.

Substance / P,MPa	S2N5OH	S3N7OH	S4N9OH	S5N11OH	S6N13OH	S7N15ON
0.1	3.22	3.20	3.14	3.11	3.07	3.04
20	3.17	3.15	3.08	3.04	3.03	3.02
40	2.90	2.86	2.86	2.84	2.76	2.72
60	2.58	2.56	2.56	2.59	2.57	2.46
80	2.51	2.48	2.47	2.42	2.36	2.20
100	2.42	2.37	2.32	2.26	2.21	2.12
150	2.06	2.06	2.00	1.93	1.90	1.77
200	1.77	1.73	1.67	1.64	1.55	1.45

As can be seen from the results obtained, with an increase in pressure and molecular weight of alcohols, the volume of micro voids between the molecules of the liquid decreases. This is fully consistent with the main provisions of the hole theory of J.I. Frenkel.

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