FINE STRUCTURE OF THE SCATTERED LIGHT SPECTRUM IN AQUEOUS SOLUTIONS WITH A PECULIAR POINT

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The peculiar point of a thermodynamically unstable solution has been little studied theoretically or experimentally, although it represents an important object for the modern physics of phase transitions and critical phenomena, as well as for the physics of liquid states in general. The conditions and physical mechanisms leading to the emergence of a peculiar point have not yet been definitively established. Consequently, the nature of fluctuation processes in the vicinity of the peculiar point has not been clarified [1].

It is currently assumed that the peculiar point of a binary solution is genetically linked to the double critical point [2]. The latter, in turn, is due to the possibility of the simultaneous occurrence of upper (UCSP) and lower (LCSP) critical stratification points in solution, the distance between which (in temperature) depends on external conditions (pressure or the presence of a third component in the solution in very small quantities).

It is assumed that the formation of the LCSP can occur due to the structural rearrangement of the solution due to such non-specific intermolecular interactions as hydrogen bonding. The theory of paired hydrogen bonds [3] qualitatively explains this phenomenon in some binary systems. However, experimental studies by Fabelinskii et al [4] revealed a number of features that cannot be explained by the theory.

In this regard, the study of systems in which a peculiar point of thermodynamic instability may exist is relevant. In this regard, the small class of currently known aqueous solutions of non-electrolytes with peculiar points (in particular, acetone, pyridine, and methyl derivatives of pyridine) is of significant interest. Unlike non-aqueous systems, hydrogen bonding in aqueous solutions of non-electrolytes cannot initially be considered an insignificant contribution to the nature of the intermolecular interactions of the system's components. The emergence of structural instability in the solution (structural phase transition) due to a change in the priority of intermolecular interactions may determine the very existence of a peculiar point in the solution. This hypothesis requires experimental confirmation.

In this paper, we discuss the results of the first study of the frequency shift of the fine structure components of the scattered light spectrum (Mandelstam-Brillouin components) $\Delta\nu$ in aqueous solutions of 4-methylpyridine (4MP) with a peculiar point depending on temperature and concentration.

Fine structure spectra were studied in pure 4MP and in its aqueous solutions with concentrations x from 0.005 to 0.8 mole fractions (m.f.). The temperature t of the solutions

varied from ~10 to ~80 °C. Analysis of the obtained values of the frequency shift of the MBC Δν shows that the shape of the temperature dependence Δν(*t*) differs significantly for solutions of medium and low concentrations.

In solutions with concentrations $x \geq 0.1$ m.f., a linear (within experimental error) dependence of Δν on *t* is observed. With increasing temperature, Δν decreases for each solution, i.e., the temperature coefficient of Δν(*t*) dependence is negative.

In contrast to solutions with a high content of non-electrolyte in water, for solutions of low concentrations ($x < 0.1$ m.f.), the pattern of change in the value of Δν is not described by a simple linear dependence on temperature.

In solutions with concentrations less than 0.06 m.f., at a certain temperature t_i, an inversion of the temperature coefficient of the shift is observed: at $t > t_i$, the coefficient is negative (the shift of the MBC decreases with increasing solution temperature), and at $t < t_i$, the coefficient is positive (the shift of the MBC increases with increasing solution temperature). The inversion temperature depends on the concentration *x* of the solution. As *x* decreases, the value of t_i shifts toward higher temperatures.

Figure 1 shows the overall dynamics of the change in the magnitude of the MBC shift in solutions across the entire range of temperatures and concentrations studied. The results in the figure are presented for a scattering angle of 90°.

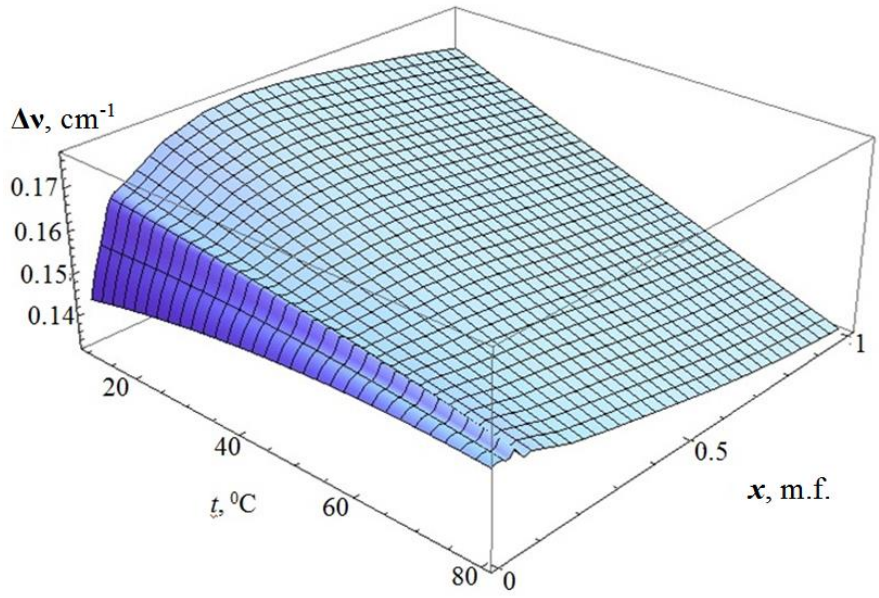

Fig.1. Concentration-temperature dependence of the displacement of the MBC in aqueous solutions of 4MP. Scattering angle 90°.

In the solutions we studied, the fine structure in the spectrum arises as a result of the modulation of scattered light by hypersonic waves with frequencies of ~4 GHz. A generally similar pattern is observed for a scattering angle of 135° (the frequency of hypersonic waves with frequencies of ~6 GHz) [5]. The independence of the sound frequency of such effects as the presence and values of the inversion points of the signs of the derivatives of the MBC shift with respect to temperature and concentration is due to processes occurring in solutions on scales significantly exceeding the hypersonic wavelength Λ (i.e., essentially globally throughout the system).

Based on the continuum model of the structure of pure water [6, 7], the patterns of change in the magnitude of the MBC shift in the studied solutions can be explained as follows.

At a fixed temperature, when the intensity of thermal motion of molecules remains unchanged, a gradual increase in concentration, i.e. the introduction of non-electrolyte molecules into the cavities of the hydrogen bond network of water, leads to strengthening of the latter and, consequently, to an increase in its elasticity. The elasticity of the network will increase as long as its three-dimensional integrity is maintained, i.e., up to a certain "critical" concentration of non-electrolyte molecules in water.

Going beyond the critical concentration leads to the continuous network of hydrogen bonds beginning to break down (fragment).

A further increase in the concentration of the non-electrolyte leads to increasing fragmentation of the network and, consequently, to a monotonic decrease in the elasticity of the solution. An increase in temperature leads to an increase in the intensity of thermal motion of both water molecules and 4MP molecules (the number of thermal defects in the network increases), and, accordingly, the process of destruction of the integrity of the network begins at lower concentrations. For this reason, the critical concentration, which accounts for the maximum elasticity of the solution, shifts to the region of lower concentrations with increasing temperature.

Thus, for the first time, an unambiguous correlation has been experimentally established between the dynamics of changes in the fine structure of the scattered light spectrum and the processes of restructuring of solutions with changes in temperature and concentration.

It should be kept in mind, however, that the magnitude of the MBC shift in the scattered light spectrum is a parameter indirectly related to the liquid structure. For this reason, temperature-concentration studies of $\Delta\nu$ provide highly valuable, but generally qualitative, information. To accurately determine the boundaries of the existence of regions with different structures in solutions, it is necessary to study the thermodynamic parameters directly related to the liquid structure.

The results obtained in the study of the fine structure spectrum for aqueous solutions of 4MP indicate the high information content of the method of fine structure spectroscopy of scattered light in the identification and study of the processes of structure formation and self-organization of molecules in liquids, as well as the promise of its application for the detection and study of structural transitions in pure liquids and solutions.

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