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Analyzing the acoustic spectra of sound velocity and absorption in amphiphilic liquids

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Abstract

The paper analyzes the theoretical approaches to the study of the acoustic spectrum and the speed of sound absorption in the frequency range up to 10 GHz in liquid systems. For example ethoxylated derivatives of normal decyl alcohol EDDn, belonging to nonionic surfactants showed that at room temperature and low degrees of ethoxylation *n* acoustic spectra can be described in terms of the relaxation theory. It is shown that within the experimental error of the acoustic spectrum of EDD*n*, in the studied range of frequencies and temperature, are composed of two prime areas of acoustic dispersion. The results of calculations of relaxation and thermodynamic parameters of fast and ultrafast processes of restructuring EDD*n* can be used in the development of combined technologies of enhanced oil recovery using surfactant solutions and various physical fields and factors.

Keywords: Acoustic spectrum; Sound velocity and absorption; Nonionic surfactant.

1. Introduction

An analysis of scientific literature has shown that methods of chemical kinetics drawing physical parallels [1,2] are currently used to theoretically describe and interpret the experimental results obtained through studying the structural transformation processes in amphiphilic liquids (i.e., liquids containing both polar and nonpolar groups), e.g., in surfactants and their solutions. For example, the Aniansson and Wall model [3] for theoretically describing micelle formation assumes that the process as a whole is similar to reaching thermal equilibrium in a thin metal rod with two massive ends. However, as noted by the authors of Ref. [4], this analogy is not perfect, since it does not reveal the molecular mechanism of the structural transformation processes in surfactants and their solutions. In addition, by now a lot of experimental data has been accumulated on acoustic, dielectric and Raleigh spectra of liquid hydrocarbons, alcohols, and phenol solutions that are fragments of many types of surfactants. A comprehensive analysis of this data conducted by relaxation spectroscopy methods has allowed to clarify the molecular mechanisms in a number of fast and ultrafast processes happening during thermal molecular motion in these liquids [4,12]. However, these mechanisms in amphiphilic liquids are under-researched. To analyze the molecular mechanisms of structural transformation of surfactants and their solutions it is necessary to employ other theoretical approaches. The reason for this is that in these systems, fast and ultrafast processes

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occur not only in homogeneous sites but in micellar heterogeneities as well.

2. Theoretical methods of analyzing the acoustic spectra of liquids

Acoustic spectroscopy for liquids studies the rate and the degree of sound absorption depending on acoustic frequency. The analysis of acoustic spectra produces data on fast and ultrafast molecular processes occurring in liquid systems during thermal molecular motion. The currently existing methods allow measuring the acoustic spectra of liquid systems in a frequency range up to 10 GHz [5–7]. The theoretical foundations of wave propagation in liquids are discussed in detail in Refs. [8,9]. We will only touch upon this problem and provide a brief review of the methods for analyzing acoustic spectra.

2.1. The equations of the classical theory of sound

According to the classical theory of sound [5,9], the amplitude absorption coefficient of longitudinal acoustic waves α in liquids is expressed in the following way:

$$\alpha = \frac{\omega^2}{2\rho c_0^3}\left\{\frac{4}{3}\eta_S + \eta_v + \chi\left(\frac{1}{c_v} + \frac{1}{c_p}\right)\right\}, \tag{1}$$

where c_v and c_p are the specific heat capacities at constant volume v and pressure p;

η_S and η_v are the shear and the bulk viscosities; χ is the thermal conductivity; $\omega = 2\pi f$ is the cyclic (circular) frequency of sound (f is its frequency); ρ is the density of unperturbed liquid; c_0 is the speed of sound in the liquid on frequencies well below the relaxation process frequency.

It follows from the classical theory of sound absorption that if the absorption is low and the frequency ω is not too high, i.e. when $\alpha\Lambda \ll \pi$ (Λ is the acoustic wavelength), then the speed of sound should not depend on the frequency, in other words, there should be no dispersion to observe. The speed of sound follows Laplace's equation:

$$c_0 = \frac{\omega^2}{K^2} = \frac{1}{\rho\beta_S}, \tag{2}$$

where β_S is the adiabatic compressibility, K is the wavevector magnitude.

If we assume that $\eta_v = 0$, then it follows from Eq. (1) for non-metallic liquids that at frequencies up to 10 GHz the term

$$\chi\,(c_v^{-1} + c_p^{-1})$$

is small (compared to the viscosity η_S) and it can be neglected [5,9]. Then for the coefficient α, which is called classical (α_{cl}), we shall obtain the expression:

$$\alpha_{cl} = \left(3\rho c_0^3\right)^{-1} 2\omega^2\eta_S, \tag{3}$$

We should note that shear viscosity is measured by viscometric methods. As for the experimentally obtained α value, it turns out to be significantly larger than that of the absorption coefficient α_{cl} calculated from Eq. (3). The difference between the measured (α) and the classical (α_{cl}) absorption coefficients is called the excess absorption coefficient α_{exc}:

$$\alpha_{exc} = \alpha - \alpha_{cl} = \frac{2\pi^2 f^2}{\rho c_0^3}\eta_v. \tag{4}$$

Using the measured values of α and η_S we can calculate the bulk viscosity:

$$\eta_v = \frac{4}{3}\eta_S\frac{\alpha - \alpha_{cl}}{\alpha_{cl}}. \tag{5}$$

The results of the experimental ultrasound studies [10–12] show that most liquids possess a bulk viscosity. Therefore, the conclusions of the classical theory of sound propagation are not, in most cases, confirmed experimentally.

2.2. The basic principles of the thermodynamic of acoustic relaxation in liquids

The main discrepancies between the classical theory of sound and the experiments were explained by the thermodynamic theory of acoustic relaxation in condensed media [10–12]. This theory claims that relaxation time (i.e., a system returning to an equilibrium state), for the given external conditions, depends on the elementary processes occurring in the studied liquid systems during thermal molecular motion. These elementary processes, which can be described in terms of chemical reactions, are molecular association, formation of molecular complexes in single-component fluids, the excitation and deexcitation processes of molecular vibrational states, rotational isomeric molecular transformations, etc.

Generally, for non-ideal solutions [12], the relaxation time depends on the kinetics and the mechanism of a reaction:

$$\tau_{pT}^{-1} = k_1 v \prod_i a_{0i}^{\upsilon i} \sum_i \Delta\upsilon_i \left(\frac{\partial \ln a_i}{\partial \xi}\right)_{T,p,\xi=0}, \tag{6}$$

where ξ is the extent of reaction, k_1 is the on-rate constant, a_i are the reagent activities, $\Delta\upsilon_i$ is the difference between stoichiometric coefficients, τ_{pT} is the relaxation time at constant pressure p and temperature T.