MOLECULAR MECHANISM OF RELAXATION ABSORPTION OF ULTRASONIC WAVES IN AN AQUEOUS SOLUTION OF CALCIUM ACETATE

Abstract. The absorption of ultrasonic waves in the frequency range from 6 to 146 MHz in aqueous solutions of sodium acetate, sodium chloride and calcium has been studied. It was found that only in solutions of calcium cations and acetate anion present simultaneously, relaxation absorption of ultrasonic waves is observed. The experimental data obtained indicate that the observed relaxation absorption of ultrasound in the studied frequency range by an aqueous solution of calcium acetate is associated with the interaction of the acetate anion with the calcium cation in the solution.

Keywords: absorption of ultrasonic waves, calcium acetate, aqueous solution, relaxation, molecular mechanism.

Measurements of the propagation velocity and the amplitude value of the absorption coefficient of ultrasonic waves (US) were carried out by us, on a pulsed...
ultrasonic installation in the frequency range from 6 MHz to 146 MHz at a
temperature of 293 K. A frequency dependence was found in aqueous solutions
of acetates of double-charged cations [1]. For calcium acetate, the excess
absorption is clearly expressed at concentrations above 0.2 mol / l. The
experimental results are fairly well described by the relaxation equation with a
single relaxation time:

\[
\frac{\alpha}{f^2} = B + A \left[ 1 + \left( \frac{f}{f_m} \right)^2 \right]^{-1},
\]

(1)

where A is a parameter that depends on the equilibrium characteristics; B
is a term that includes the classical absorption and the contribution from any
other relaxation processes that have characteristic frequencies much higher than
the relaxation frequency (f_m).

The analysis of the literature data and our studies show that relaxation
absorption of US occurs in aqueous solutions of acetates of double-charged
cations. Various mechanisms of relaxation absorption are assumed (relaxation
of the degree of dissociation, relaxation of ionic atmospheres, stepwise
withdrawal of the water molecule from the hydrate shell of the ion, etc. [2-8].
Moreover, these assumptions are not unambiguous and require further
research.

Although the phenomenological relaxation theory describes the frequency
dependence of the absorption coefficient quite well, it cannot specify a specific
mechanism of the relaxation process. To clarify the features of a particular
relaxation process, an important role is played by the study of its molecular-
kinetic mechanism.

From the molecular-kinetic point of view, various processes of establishing
equilibrium are considered as a mechanism of the relaxation process (energy
redistribution between internal and external degrees of freedom of molecules;
relaxation due to rearrangement of molecules under the action of
ULTRASOUND (US) – structural relaxation; formation and decay of various
complexes under the action of ultrasound in solution, etc.). In electrolyte solutions, relaxation absorption can be caused by various reasons.

In solutions containing polyatomic ions, thermal relaxation can be expected due to the excitation of intramolecular degrees of freedom. Since the probability of excitation of the molecular degree of freedom does not depend on the concentration, in this case the dependence of the absorption on the concentration should be linear. However, our data show a disproportionate increase in absorption with increasing concentration.

Another possible relaxation process is the relaxation of ionic atmospheres, which occurs as a result of the electrostatic interaction of ions. First, the relaxation of ionic atmospheres can be expected in strong multicharged electrolytes at high frequencies [7]; second, the values of the \( f_m \) value characterizing the relaxation of ionic atmospheres should strongly depend on the concentration of the electrolyte [2].

The results obtained by us do not agree with the conclusions of the theory of relaxation of ionic atmospheres, since there is no noticeable dependence of the relaxation frequency on the concentration. The absorption associated with the relaxation of ionic atmospheres is very small [2].

Another possible mechanism of relaxation absorption is the disturbance of the equilibrium hydrate shell of ions by an ultrasonic wave. Since the hydration reaction, even at high concentrations, is a reaction of the 1st order, there should be a linear increase in excess absorption with increasing concentration, which is not observed in the experiment. In addition, solutions with the same ions should have similar values of the absorption coefficient and relaxation times. To test this assumption, we investigated the absorption of US in aqueous solutions having the same \( \text{CaCl}_2 \) u Ca cations \((\text{CH}_3\text{COO})_2\), and the same anions of \( \text{CH}_3\text{COONa} \) u Ca(\( \text{CH}_3\text{COO} \)_2. The results of measuring the ultrasonic absorption coefficient in the frequency range from 6 to 146 MHz for aqueous solutions of calcium chloride (0.8 mol/l) at different temperatures are shown in Figure 1.
Fig. 1. The dependence of the value on for an aqueous solution of calcium chloride concentration of 0.8 mol/l at various $T, K$: 1-293, 2-303, 3-313 and 4-323

The results of measuring the ultrasonic absorption in aqueous solutions of sodium acetate and calcium having the same anion concentrations at 293 K are shown in Fig. 2. From the comparison of these figures, it can be seen that the absorption of US strongly depends on the anion and cation. In an aqueous solution of sodium acetate, the absorption is the same as in pure water, and in an aqueous solution of calcium acetate, it has a relaxation character. It follows that the type of relaxation absorption-ion-solvent relaxation for an aqueous solution of calcium acetate also disappears.

Fig. 2. Dependence of the $\alpha t$ value for aqueous solutions of sodium acetate (1.6 mol/l) -1 and calcium acetate (0.8 mol/l) -2 at 293 K.
Currently, many researchers believe that the relaxation processes observed in electrolyte solutions are caused by a violation of the association – dissociation equilibrium under the action of ultrasound [2,3]. Therefore, the absorption of US in an aqueous solution of a mixture of 0.8 mol/l \( \text{CaCl}_2 \) and 1.6 mol/l \( \text{CH}_3\text{COONa} \) was studied. The choice of the concentration of the components was determined in order to obtain a solution in which the ion concentrations corresponded to the concentrations of \( \text{Ca}^{2+} \) and \( \text{CH}_3\text{COO}^- \) ions of the 0.8 mol/l aqueous solution of calcium acetate studied by us [1].

Our studies have shown that, in contrast to solutions composed of individual components of mixtures, in solutions containing both \( \text{CaCl}_2 \) and \( \text{CH}_3\text{COONa} \), there is a noticeable relaxation absorption of US (Fig. 3). Obviously, this absorption of US is due to the presence of \( \text{Ca}^{2+} \) and \( \text{CH}_3\text{COO}^- \) ions in the solution. When calculating the relaxation parameters from the experimental data \( (a/f)^2 \) for the mixture, the contribution of the absorption of calcium chloride was subtracted. The difference \( (a/f)^2 \) for different frequencies is well described by the formula (1). The values of the relaxation parameters found are as follows: \( A = 223 \cdot 10^{-15} \text{ m}^2 \text{s}^2 \); \( B = 48 \cdot 10^{-15} \text{ m}^2 \text{s}^2 \) and \( f_m = 59 \text{ MHz} \).

![Dependence of the value on for aqueous solutions of NaCl (C=1.6 mol/l) and NaCH₃COO (1.6 mol/l) -1; CaCl₂ (0.8 mol/L) -2 and NaCH₃COO (1.6 mol/l) + CaCl₂ (0.8 mol/l)-3. at 293 K](image)
Let us consider which processes are responsible for the relaxation absorption in a given frequency range. When the CaCl$_2$ and CH$_3$COONa salts are dissolved in water, the following ions are formed: Ca$^{2+}$ +2Cl$^-$ + CH$_3$COO$^-$ + Na$^+$. From the data in Figures 1 and 2, it can be seen that, separately, aqueous solutions of CaCl$_2$, CH$_3$COONa, and NaCl cannot be the cause of the observed relaxation absorption.

Hence, taking into account the results obtained, we can assume that associates of C1$^-$.C$^{2+}$ and CH$_3$COO$^-$.C$^{2+}$ ions can be formed in the solution, and excessive absorption of US in an aqueous solution of calcium acetate is associated with a violation of the equilibrium concentrations of these associates, i.e., with the interaction of the calcium cation and the acetate anion.

Next, we studied mixtures of CaCl$_2$ and CH$_3$COONa of different ratios. The study of such mixtures in the frequency range, including the relaxation region, makes it possible to find out the influence of the concentration of anions and cations on the course of the relaxation process and to trace a number of features of its course. The results obtained confirm our conclusion that in the range from 6 to 146 MHz, the relaxation absorption of ultrasound in the mixture is characteristic of an aqueous solution of calcium acetate. The values of the relaxation parameters found are given in Table 1.

Table 1

<table>
<thead>
<tr>
<th>$\rho$, kg/m$^3$</th>
<th>A · 10$^{15}$, m$^1$s$^2$</th>
<th>B · 10$^{15}$, m$^1$s$^2$</th>
<th>$f_m$, MHz</th>
<th>$\varphi$, m/s</th>
<th>$\alpha$ (max), 10$^{-3}$ dB</th>
<th>C$_1$ + C$_2$, mol/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1097,6</td>
<td>78</td>
<td>55</td>
<td>59</td>
<td>1637</td>
<td>3,8</td>
<td>0,8+0,8</td>
</tr>
<tr>
<td>1131,8</td>
<td>234</td>
<td>57</td>
<td>59</td>
<td>1679</td>
<td>10,6</td>
<td>0,8+1,6</td>
</tr>
<tr>
<td>1151,6</td>
<td>364</td>
<td>72</td>
<td>59</td>
<td>1729</td>
<td>13,5</td>
<td>0,8+2,4</td>
</tr>
<tr>
<td>1160,3</td>
<td>95</td>
<td>67</td>
<td>59</td>
<td>1697</td>
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<td>1,6+0,8</td>
</tr>
<tr>
<td>1201,0</td>
<td>346</td>
<td>90</td>
<td>59</td>
<td>1753</td>
<td>17,9</td>
<td>1,6+1,6</td>
</tr>
</tbody>
</table>

As can be seen from the table, the relaxation frequency does not depend on the ratio of the concentration of the components of the mixtures in the solution.
and is the same as in an aqueous solution of calcium acetate. When the concentration of sodium acetate and a constant concentration of CaCl₂, as well as the simultaneous increase of the parameter A increases greater than in the case of constant concentration CH₃COONa and the concentration of CaCl₂.

It was of interest to find out how the presence of an excess of CH₃COO anions in a solution of calcium acetate affects the absorption of ultrasound and the relaxation time. For this purpose, it was necessary to choose an inert electrolyte that must meet the following requirements: it must be a strong electrolyte;

- the cation of the inert electrolyte should not associate with the anion; the solubility of the electrolyte should be sufficiently large; the contribution of the electrolyte to the measured absorption of the ultrasound should be negligible.

Among the small number of salts that meet these requirements, the most suitable was an aqueous solution of sodium acetate.

In order to determine the effect of the concentration of the acetate anion, the absorption of US in mixtures of calcium acetates (0.4 mol/l) and sodium of various concentrations (0-3.2 mol/L) was studied. The measurements were carried out at a temperature of 293 K.

The results are shown in Fig. 4. As can be seen from the figure, the relaxation frequency (59 MHz) and the value $B = 57 \times 10^{-15} \text{ m}^{-1} \text{ s}^2$ do not depend on the concentration of the anion in the solution. In this case, the parameter $A$ increases from $124 \times 10^{-15} \text{ m}^{-1} \text{ s}^2$ to $224 \times 10^{-15} \text{ m}^{-1} \text{ s}^2$. The absorption parameter $B$ is determined by the structure of the solvent.

In order to / l Ca (CH₃COO)$_2$ + 0.8 mol/l CH₃COONa and 0.4 mol/l Ca(CH₃COO)$_2$ + 1.2 mol / l CH₃COONa at T = 293 K on a hypersonic installation at a frequency of 670 MHz. The results obtained within the margin of error of the experiment (±7%) coincide with verify the reality of the value B calculated by the graphical method, we carried out control measurements of this value for aqueous solutions of mixtures of 0.4 mol each other.
Fig. 4. Dependence on for aqueous solutions of a mixture of 0.4 mol/l Ca(CH$_3$COO)$_2$ and CH$_3$COONa of different concentrations (mol/l) at 293 K: 1-0.2; 2-0.4; 3-0.6; 4-0.8; 5-1; 6-1.2; 7-1.4

Based on the experimental data obtained, it can be assumed that the observed relaxation absorption of ultrasound in an aqueous solution of calcium acetate in the frequency range from 6 MHz to 146 MHz is associated with the interaction of the CH$_3$COO$^-$ anion with the Ca$^{2+}$ cation in the solution.

References: