ON ULTRASONIC RELAXATION STUDY OF PREFERENTIAL SOLVATION IN QUASI TWO-COMPONENT AQUEOUS SOLUTIONS OF AMIDES AND ZINC SALTS

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To investigate the effect of preferential solvation, the ultrasonic attenuation (2–50 MHz) and velocities (3 MHz) in $ZnCl_2$ and 2-chloroacetamide ($ClCH_2CONH_2$) solutions in water and its quasi-binary mixtures of the ratio ($ZnCl_2 + ClCH_2CONH_2$): $H_2O = 1 : 55$ at 298.15 K have been measured. The creation of specific complexes in the $ClCH_2CONH_2 - H_2O - ZnCl_2$ system have a relaxational character which, within the measurements of the ultrasonic absorption in the frequency range 2–50 MHz, have been observed. On the base of these properties, the kinetic and dynamic parameters of the observed relaxation have been calculated. To bring into relief the influence of the Cl atom in the 2-chloroacetamide molecules for the complexation process, also the system $AA - H_2O - ZnCl_2$ has been investigated. The next step of searching was the investigation of the system of $CHAA - H_2O - ZnBr_2$, to reduce the influence of the Cl atom within the $ZnCl_2$ molecule in the complexation process. As the results, the observed relaxation processes have been attributed to the creation and disintegration of the following complexes: $Zn(H_2O)_2(CHAA)_4^{2+}$ and $Zn^{2+}(H_2O)_3(CHAA)Cl_2^-$.

1. Introduction

Preferential ion solvation in mixed solvent systems is an interesting phenomenon playing an important role in the solubility and kinetics. The solvent exchange reaction is one of the most basic chemical reactions of metal ions in solution, and its mechanism has been widely investigated in order to characterise the reactivity of the metal ion.

Interactions between solute and solvent in multi-component liquid mixtures have been the subject of numerous studies in the solution chemistry. An interesting aspect of binary mixed solvent/electrolyte systems is the possibility of the enrichment of either of the two solvents in the solvation shells of the ions leading to characteristic deviations of the solution properties from a linear dependence upon the mixture composition [1–3].

The earliest investigations of electrolyte solutions focused on aqueous systems and single organic solvents [4, 5]. Relative little attention has been focused on the problem of ion solvation in binary mixtures, although there have been some experimental studies

carried out on such systems [6]. The latter find application in various technologies as they offer a wide choice of solutions with appropriate properties.

Information on electrolyte solutions in binary mixed solvents has so far come mainly from the use of thermodynamic, viscosimetric, electrochemical, and other macroscopic methods. Only few spectroscopic investigations of these systems have been carried out. One of this is an ultrasonic spectrometry study that was used in the reported investigations. The measurement of ultrasonic absorption is useful for probing the microscopic solution structure and may be used to study relaxation processes with characteristic time constant of $10^{-5} - 10^{-10}$ sec. The types of various molecular processes which lead to sound absorption, predominantly stoichiometrically defined reactions on the one hand side, and large fluctuations of thermodynamic and transport parameters on the other hand side are reflected in the shape of the excess absorption spectra.

A theoretical attempt has been also made to describe ternary solutions containing electrolytes [7]. A quasi-lattice quasi-chemical theory of preferential solvation of ions in mixed solvents was used to explain those properties of electrolyte solutions in solvent mixtures that deviate from a linear dependence on the composition of the mixture. A very successful model for ions that have a geometrically well-defined first coordination sphere treats the two solvents as ligands competing for sites in the coordination sphere and forming a mixed-solvate complex. Many ions, however, do not form a well-defined coordination sphere or the ion itself is an ionic complex with an inner coordination sphere saturated by ligands that are not the solvent molecules, as for instance, $ZnCl_4^{2-}$. For such systems another approach would be preferable, especially the theory based on the quasi-lattice quasi-chemical model which transfer the thermodynamic data of electrolytes or of ions from a given solvent to a mixture of solvents. On the other hand, theoretical studies of preferential ligand binding are still quite rare, mostly due to the relatively high computational effort needed for the simulation of multi-component systems.

Recently, theoretical calculations and computer simulations have been reported [8]. Most of the simulations of the solvation in mixture were aimed at the investigation of equilibrium properties [9, 10], and the dynamics of the solvation process [1].
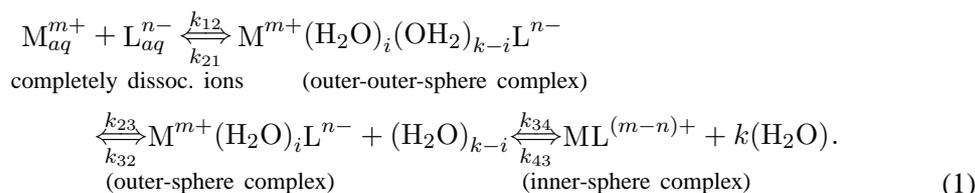
2. Characteristic of the studied solutions

$ZnCl_2$ and $ZnBr_2$ were selected to act as electrolytes. Among many electrolyte solutions, the most characteristic ones (due to their thermodynamic anomalies) are aqueous solutions of zinc salts. In this group of particular notice are aqueous solutions of zinc chloride. In concentrated solutions self-complexation takes place, and beside the totally dissociated ions they also contain mono-di-, tri-, and tetrachloro-complexes of $ZnCl_4^{2-}$ [11, 12]. In more dilute solutions the zinc ion Zn^+ is surrounded by a hydration layer forming different type of hydration ions. On the other hand, it was suggested that aqueous 2.88 M solutions $ZnCl_2$ in 9.35M HCl, or even more dilute solutions which are formed after adding organic solvents [DMF, CH_3OH, $(CH_3)_2SO$], reach an equilib-
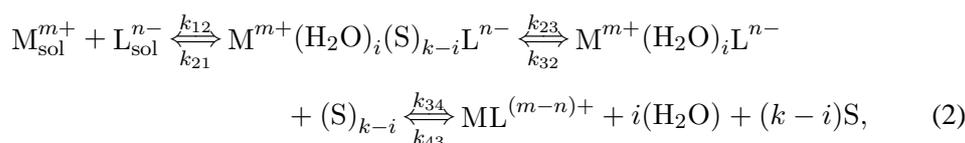
rium between the hexagonal and tetragonal geometry [13]. Generally, zinc has the most adaptable coordination sphere: it behaves like a "chameleon" [14].

More and more attention is paid at present to the mechanism of intermolecular interactions between water and amides [15–17]. It is generally known from thermodynamics [18, 19], NMR spectroscopy [20] and other methods that one-substituted amides form chain multimers in the liquid state due to the occurrence of intermolecular hydrogen bonds. The amide group has a strong electron-donor property. On the other hand side the H atoms in the NH_2 group play the role of electron-acceptor centres of the type AA•AA (AA – acetamide). The donor-acceptor function of the amide molecule is partly responsible for the strong association of the liquid acetamide (CH_3CONH_2). One can speak about self-association in acetamide where strong bounded dimmer-rings should be present. In the case of 2-chloroacetamide ($ClCH_2CONH_2$), strong hydrogen bond between the molecules of amides could also be expected.

As a result of many studies on complexation between M^{m+} cations and ligands L^{zL} in pure aqueous solutions the following scheme of the reaction has been proposed. Initially, owing to the diffusion, a hydrated ion forms an outer-outer sphere complex. Both the metal ion and ligand are hydrated. Thus ions become separated by two layers of solvent molecules. In the next step, only the cation hydration layer separates both ions (the outer sphere complex). In the third and last phase, which might be quite slow, inner sphere complexes are finally formed. The ions can be in a direct contact with one another. These reactions can be presented according to the scheme proposed by EIGEN [21]:

$$M_{aq}^{m+} + L_{aq}^{n-} \underset{k_{21}}{\overset{k_{12}}{\Longleftrightarrow}} M^{m+}(H_2O)_i(OH_2)_{k-i}L^{n-}$$

completely dissoc. ions   (outer-outer-sphere complex)

$$\underset{k_{32}}{\overset{k_{23}}{\Longleftrightarrow}} M^{m+}(H_2O)_i L^{n-} + (H_2O)_{k-i} \underset{k_{43}}{\overset{k_{34}}{\Longleftrightarrow}} ML^{(m-n)+} + k(H_2O).$$

(outer-sphere complex)   (inner-sphere complex)

$$(1)$$

If, however, we take into account an electrolyte solution containing a binary solvent, then under some condition the composition of solvation sheath will change. The previous scheme for aqueous solutions may be written as follows:

$$M_{sol}^{m+} + L_{sol}^{n-} \underset{k_{21}}{\overset{k_{12}}{\Longleftrightarrow}} M^{m+}(H_2O)_i(S)_{k-i}L^{n-} \underset{k_{32}}{\overset{k_{23}}{\Longleftrightarrow}} M^{m+}(H_2O)_i L^{n-}$$

$$+ (S)_{k-i} \underset{k_{43}}{\overset{k_{34}}{\Longleftrightarrow}} ML^{(m-n)+} + i(H_2O) + (k-i)S, \qquad (2)$$

where S is the second solvent, which can be a second ligand as well.

For the cation M^{m+}, with a coordination number k and a charge $m+$, in a mixture of two solvents H_2O and S, we may expect $k + 1$ cations differently solvated within the inner solvation sphere,

$$M(H_2O)(S)_{k-i}^{m+}, \qquad \text{with} \quad i = 0 \ldots k.$$

The main aim of the study presented was to investigate the possibility of complexation in aqueous solutions of $ZnCl_2$ with the participation of 2-$ClCH_2CONH_2$ (CHAA). Because of the large complexing ability of zinc, there exists a theoretical possibility of the attachment of CHAA to the inner coordination sphere of zinc through the chloride atom. Outer-sphere as well as inner-sphere complexes can be created.

The next step of the study was to investigate the system of CHAA – H_2O – $ZnBr_2$ to reduce the influence of the Cl atom within the $ZnCl_2$ molecule at the complexation process.

In order to reduce the influence of the Cl atom in the 2-chloroacetamide molecules on the complexation process, also the system AA – H_2O – $ZnCl_2$ (AA – CH_3CONH_2) has been investigated.

Finally, the following three systems have been investigated:

A. CHAA – H_2O – $ZnCl_2$,

B. CHAA – H_2O – $ZnBr_2$,

C. AA – H_2O – $ZnCl_2$.

3. Experimental

All measurements were taken at the same temperature, i.e. $T = 298.15$ K.

Measurements of the absorption coefficient, α, were done by a pulse method with piezoelectric broadband transducers (frequency range 2–50 MHz) and an electronic equipment of MATEC 7700. The coefficient α was determined from the amplitude decay over a certain path length. Here, the relative error was lower than 8% within the whole frequency range.

The speeds of ultrasonic waves were measured by the pulse-echo-overlap method using the MATEC apparatus. The block diagram of the apparatus of the first method is presented in Fig. 1. Here the ultrasonic speeds are determined by measuring the time difference between successive echoes which corresponds to the phase delay of the wave. The operation frequency of the transducers was 3.142 MHz. The relative error of the measured velocities was lower than 0.01%.

2-$ClCH_2CONH_2$ produced by MERCK Schuchardt, CH_3CONH_2 and $ZnBr_2$ produced by ALDRICH and $ZnCl_2$ produced by Riedel–de Haën AG, and twice-distilled water were used for preparing the solutions. To express the concentration of the ternary solutions as mole fractions, an initial solution of the ratio of H_2O : $ZnCl_2$ ($ZnBr_2$) $= 55 : 1$ and another one of H_2O : $ClCH_2CONH_2$ (CH_3CONH_2) of the same ratio, have been prepared. The concentration in the mole fraction was defined as $x_2 = n_2/(n_1 + n_2)$ where x_2 is the mole fraction of $ZnCl_2$ (or $ZnBr_2$), n_1, n_2 are the numbers of CHAA (or AA) and $ZnCl_2$ (or $ZnBr_2$) moles, respectively. At $x_2 = 0$ we have a pure aqueous CHAA (or AA) solution and at $x_2 = 1$ a pure aqueous $ZnCl_2$ (or $ZnBr_2$) solution. At intermediate x_2 ratio of $ZnCl_2$/CHAA, $ZnBr_2$/CHAA and $ZnCl_2$/AA varies, but the amount of water remains constant (55 moles). These solutions are quasi-two-components solutions with the components:

A. n_1CHAA – 55H$_2$O – n_2ZnCl$_2$ where: $n_1 + n_2 = 1$,

B. n_1CHAA – 55H$_2$O – n_2ZnBr$_2$,

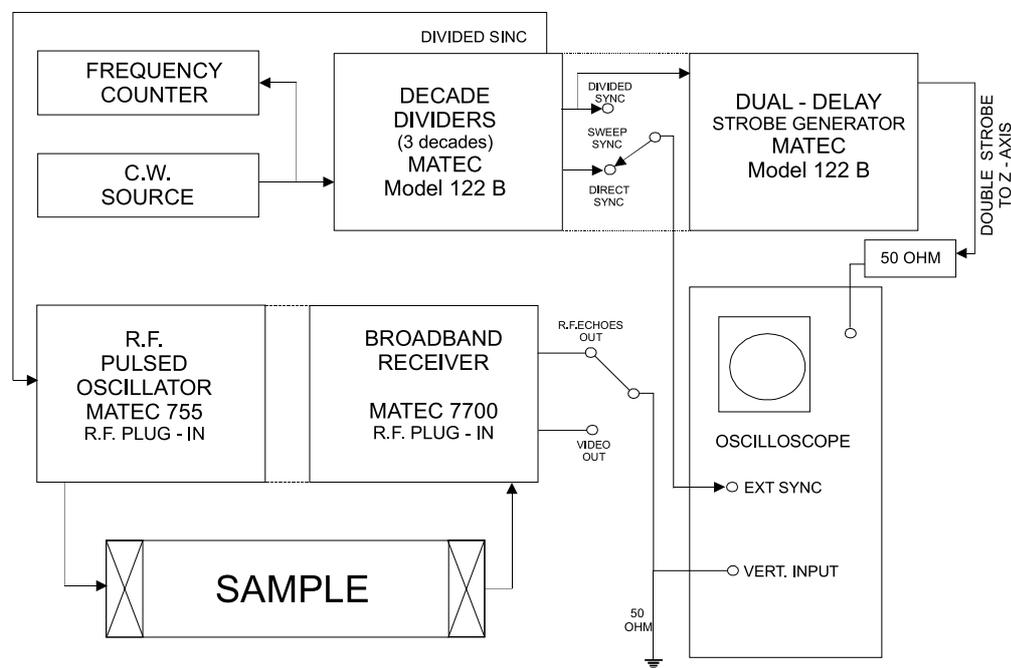C. n_1AA – 55H$_2$O – n_2ZnCl$_2$.

Fig. 1. The block diagram of the MATEC instruments.

## 4. Results and analysis

4.1. Frequency dependences

Measurements of the absorption coefficient, α, were made within the frequency range 2–50 MHz. It should be stressed that not for all concentrations the measuring range reaches the frequency of 2 MHz. Generally, the beginning of the measurements sets up from the frequency of 3 MHz. Measurements on frequencies below 3 MHz by impulse method are difficult because of the small attenuation (Figs. 2a and 2b) and a too large attenuation (Figs. 2f–2i).

To determine the kinetics and the kind of reactions responsible for the observed relaxation it the dependences of quantity α/ν^2 on frequency ν of ultrasound have been measured at carefully selected concentrations of the solution of the system CHAA – H$_2$O – ZnCl$_2$.
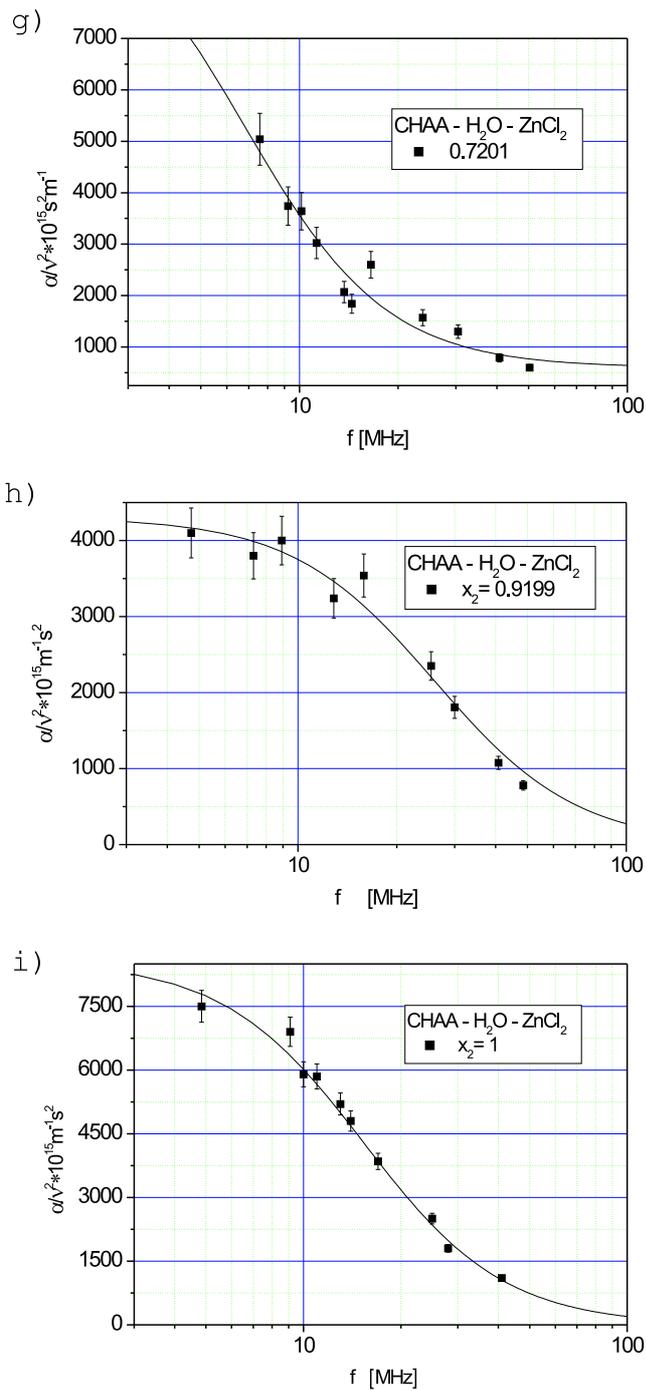
a)

b)

c)

[Fig. 2 a, b, c.]

d)

e)

f)

[Fig. 2 d, e, f.]

g)

h)

i)
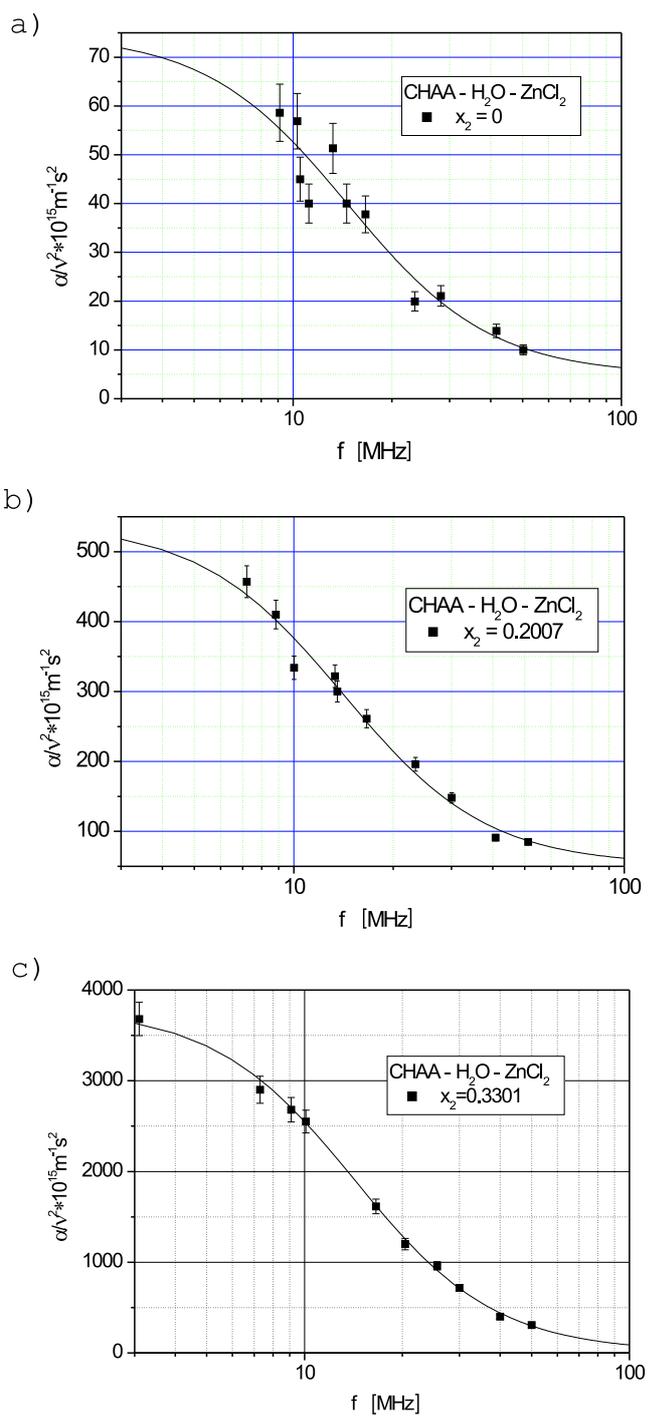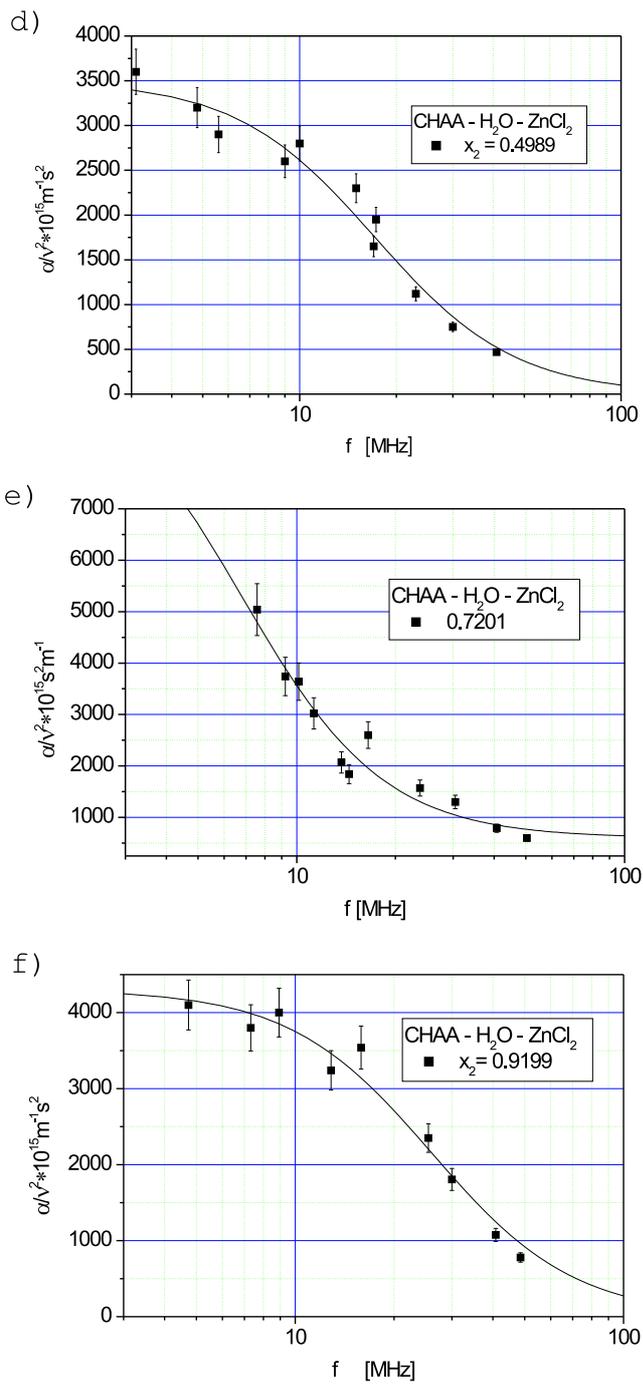
Fig. 2. The dependence of ultrasonic absorption α/ν^2 on frequency in the system CHAA H_2O – $ZnCl_2$ at the temperature 298.15 K.

The measurement results are shown in Figs. 2a–2i. The results clearly indicate a relaxation character of the sound absorption. These results are described using Debye's equation with one relaxation time,

$$\frac{\alpha}{\nu^2} = \frac{A}{1 + \left(\dfrac{\nu}{\nu_c}\right)^2} + B,$$ (3)

where ν_c is the characteristic relaxation frequency, A is a parameter characterizing the relaxation process, and B denotes a parameter characterizing the "classical absorption" and other dissipative processes for higher frequencies. Using the least-squares regression analysis method, theoretical curves of Eq. (3) were obtained (solid lines in Fig. 2). By using the above procedure, the relaxation parameters A, B and ν_c were obtained (Table 1). The errors of the values obtained result from the experimental uncertainties $\Delta\alpha(\nu_n)$ of $\alpha(\nu_n)$.

Table 1. Relaxation parameters for the $ClCH_2CONH_2 – H_2O – ZnCl_2$ system.

x_2 mole fraction	A $10^{15}m^{-1}s^2$	B $10^{15}m^{-1}s^2$	ν_c MHz	τ ns	c $m\cdot s^{-1}$	μ_{max} 10^2
0	70±12	6±6	14.7±5.0	10.8±3.7	1527.3±0.3	0.09±0.04
0.2007±0.0001	487±33	52±20	14.1±2.0	11.3±1.6	1533.6±0.3	0.53±0.11
0.3301±0.0001	3783±70	31±31	14.3±2.0	11.2±1.6	1533.0±0.3	4.14±0.66
0.4989±0.0001	3500±260	130±130	17.2±2.1	9.3±1.1	1514.3±0.3	4.55±0.89
0.5231±0.0001	2460±190	90±90	19.3±3.4	8.3±1.5	1514.2±0.3	3.58±0.91
0.6671±0.0001	7330±390	390±75	7.00±0.46	22.7±1.5	1514.5±0.3	3.89±4.62
0.7201±0.0001	9400±2800	600±190	6.8±1.7	23.6±6.0	1489.8±0.3	4.75±2.64
0.9199±0.0001	4300±470	245±245	26.1±4.3	6.1±1.0	1506.3±0.3	8.45±2.33
1	8570±410	175±175	15.4±1.6	10.4±1.1	1497.4±0.3	9.85±1.48

In order to ascertain the nature of the relaxation processes, one must begin with determining the nature of the processes in the initial solutions. It must be noted that ultrasonic dispersion takes places both at $x_2 = 0$ and at $x_2 = 1$ (Fig. 2a and Fig. 2i).

The initial solution ($x_2 = 0$) was an aqueous solution of CHAA. The relaxation process which could be noticed in this case may involve the development and disintegration of mixed complexes made of H_2O and $ClCH_2CONH_2$ molecules. The emergence of the complexes may be the result of an interaction through hydrogen bonds.

The other initial solution ($x_2 = 1$) was an aqueous solution of $ZnCl_2$. Aqueous solutions of $ZnCl_2$ deserve particular attention because autocomplexing as well as the formation of mono-, di or tetra-chlorocomplexes (depending on the concentration) have been observed beside totally dissociated ions [22]. And yet, the complex ions (both the anion and the cation) develop gradually. Thus, the reaction, which involves an exchange

of water molecules in the outer-spherical complexes, must occur in several stages. Nevertheless, the empirical observation suggests a single relaxation process within the ultrasonic frequency used. In fact, we must witness only one of several stages. As we see, it is rather difficult to account for a certain relaxation process with one reaction only.

Let us now consider the type of relaxation processes that we should expect in the case of the investigation of three-component solutions. In view of the electrolytes having a more significant impact on the characteristics of the solutions, it is most likely that the most prominent reactions will be those caused by the presence of zinc chloride in the solution. The quantities characteristic of the processes occurring in the solutions are the relaxation time τ, the parameter A and the value of the maximum absorption of ultrasounds at a certain wavelength $\mu_{\max} = (\alpha\lambda)_{\max}$. Therefore, the concentration characteristics of these quantities may provide an evidence of the nature of the processes. Basing on the numeric presentation, the relaxation parameters: $(\alpha\lambda)_{\max} = A\nu_c c/2$ and $\tau = 1/(2\pi\nu_c)$ were calculated.

The dependence of the relaxation parameter A (Fig. 3), which characterizes the amplitude of relaxation process, has two maxima for the concentrations: $x_{\max1} \approx 0.425$ and $x_{\max2} \approx 0.75$.

The relaxation time τ (Fig. 4), in spite of the rather big error of evaluating, shows a second maximum for $x_{\max2}$. The relaxation time for the first relaxation ($x_{\max1}$) is similar to that one of the initial concentrations. Different from this runs, the dependence of $\mu_{\max}$ on concentration (Fig. 5), demonstrates the maximum at $x_{\max1}$ (the second one is difficult to ascertain due to the big error of evaluating).
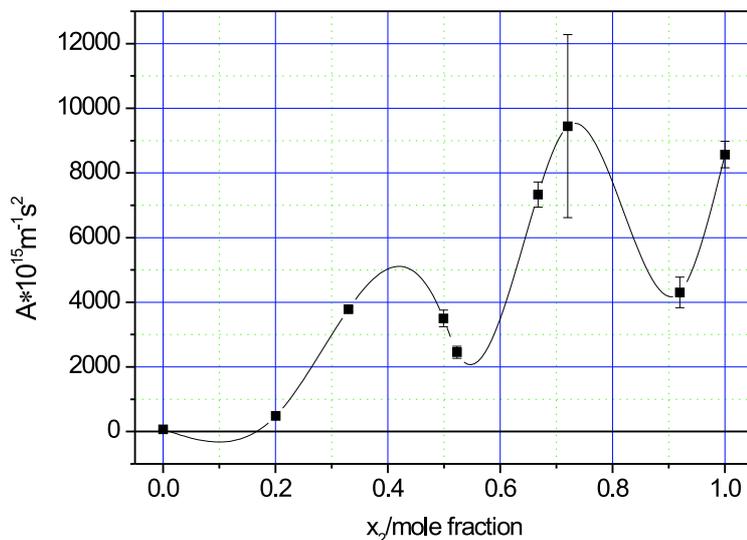

Fig. 3. The dependences of the relaxation parameter A on concentration in the system CHAA–H_2O–$ZnCl_2$ at the temperature 298.15 K.
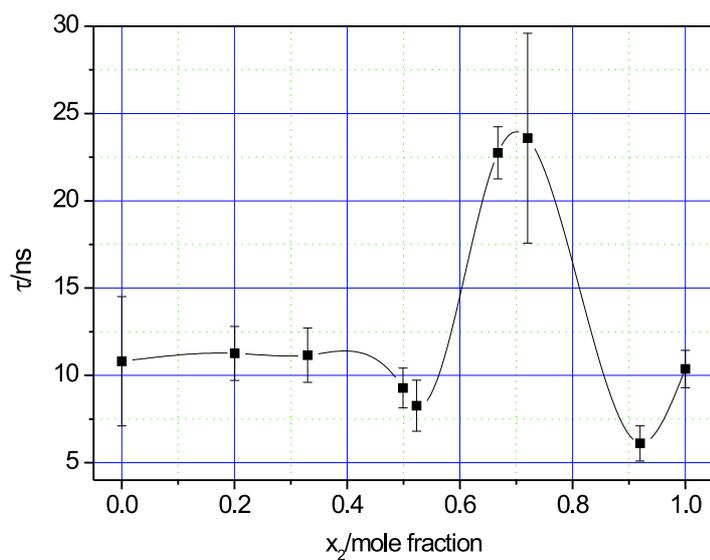
Fig. 4. The dependences of the relaxation time τ on concentration in the system CHAA – H_2O – $ZnCl_2$ at the temperature 298.15 K.
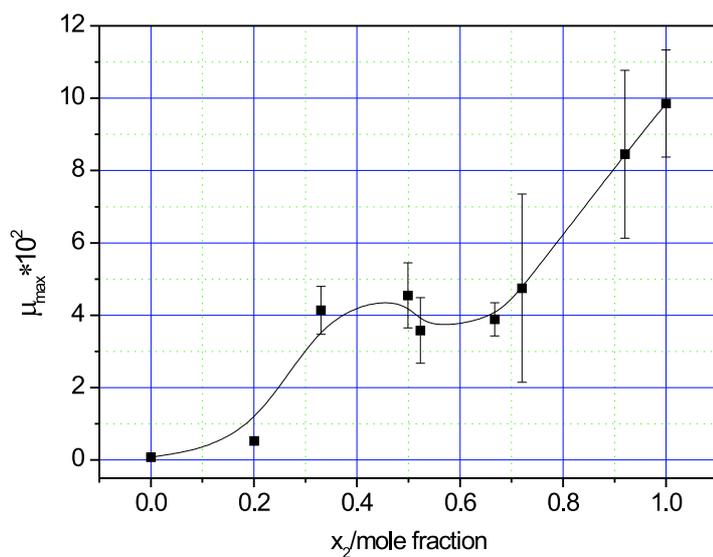

Fig. 5. The dependences of μ_{max} on concentration in the system CHAA – H_2O – $ZnCl_2$ at the temperature 298.15 K.

4.2. Concentration dependences

Measurement results of α as the dependence of the value α/ν^2 on concentration for the three different systems are shown in the Figs. 6–8.
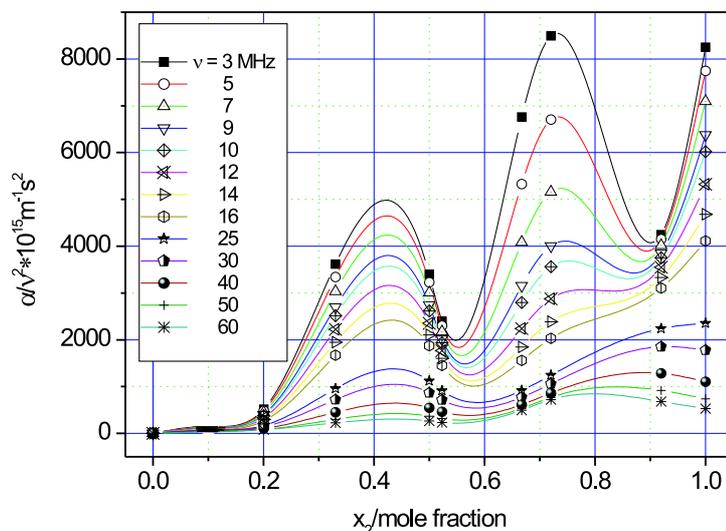
A. The system CHAA – H_2O – $ZnCl_2$ (Fig. 6).

Fig. 6. The concentration dependence of the quantity α/ν^2 in the system CHAA – H_2O – $ZnCl_2$ at the temperature 298.15 K – the points are results of the curve fitting (Formula1) to the experimental data (Fig. 2).

Analysing the dependence of the quantity of α/ν^2 on concentration for different frequencies of the acoustics waves (Fig. 2.), we can observe nonlinear runs with two maxima like for the relaxation parameter A. Here the points results from the curve fitting (Formula (3)) to the experimental data (Figs. 2a–2i). There were not the experimental points of the same ultrasonic frequency.

The observed maxima appear for the same following concentrations and its corresponding composition of solutions:

$$(1) \; x_{max1} \approx 0.425 \Leftrightarrow 4CHAA : 3ZnCl_2 : 385H_2O,$$

$$(2) \; x_{max2} \approx 0.75 \Leftrightarrow CHAA : 3ZnCl_2 : 220H_2O.$$

These phenomena point to creation of mixed complexes with the participation of $ZnCl_2$ and CHAA molecules at the same time. Additionally, the runs for the respective frequency are not coincidenced that indicate the relaxational character of the ultrasonic absorption in such of solutions described in the last section.

B. The system CHAA – H_2O – $ZnBr_2$ (Fig. 7).

In order to investigate the influence of the individual ingredients on the observed relaxation phenomena, zinc chloride has been replaced by zinc bromide. The results are illustrated in Fig. 7. Since the measurements in this system are comparative, only two relatively low frequencies, where we can expect the relaxation processes, has been chosen. The monotonic run (lack of extrema) for this system indicate the shortage of
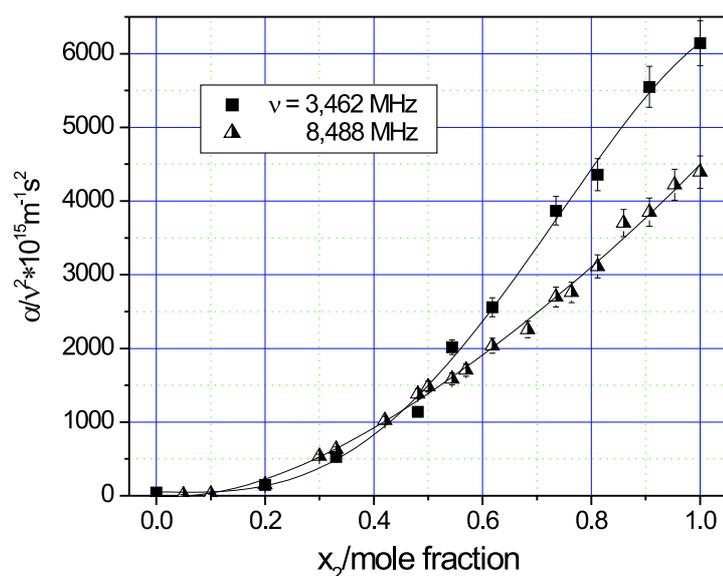
Fig. 7. The concentration dependence of the quantity α/ν^2 in the system CHAA – H$_2$O – ZnBr$_2$ at the temperature 298.15 K.

the possibilities of the creation of mixed complexes between the CHAA molecule and ZnBr$_2$ within the range of the ultrasonic frequency waves under examination. The possible relaxation process (for the whole concentration range) will be related to the creation and disintegration of autocomplexes of zinc bromide, e.g. ZnBr$_4^{2-}$, only.

What is the conclusion for the A system (CHAA – H$_2$O – ZnCl$_2$)? The relaxations, which are responsible for the two observed maxima (in the relation of $\alpha/\nu^2 = f(x_2)$ – Fig. 6) cannot be connected to the autocomplexation of zinc chloride only but to the complexation with a part of Zn and CHAA. Outer sphere complexes are possible.

C. The system AA – H$_2$O – ZnCl$_2$ (Fig. 8).

The influence of the Cl atom in the molecule of 2-chloroacetamide has been investigated through the measurement of the dependence $\alpha/\nu^2 = f(x_2)$ in the system with acetamide molecules. Since the measurements in this system are also comparative, only two relatively low frequencies, have been chosen, at which a relaxation processes can be expected. The results of measurements, illustrated in Fig. 8, indicate clearly that as in the system A a maximum appears here at the concentration x$_{max2} \cong 0.75$ mole fraction of ZnCl$_2$. The first maximum at x_{max1} is not present.

What is the conclusion for the A system (CHAA – H$_2$O – ZnCl$_2$)? It was proved that in this system the following molecules participate in the creation of complexes:

- for the x_{max1} region of concentration – Zn coordinates CHAA molecules though the Cl atom,
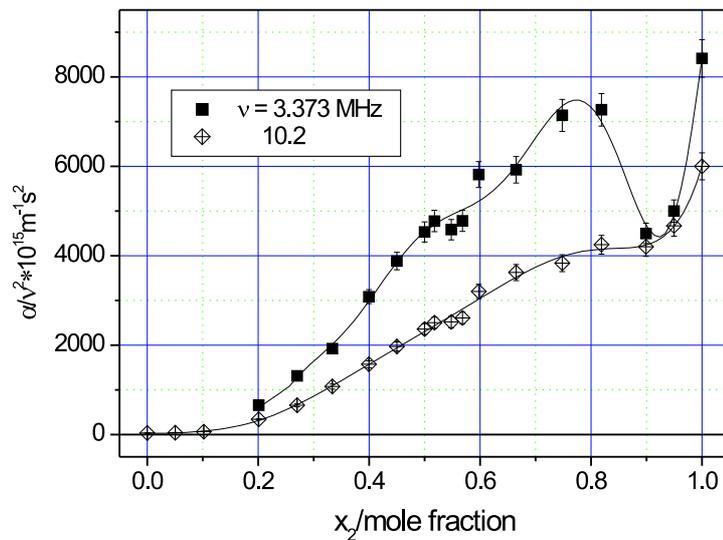- for the x_{max2} region of concentration – Zn coordinates whole CHAA molecules as a ligand.

Fig. 8. The concentration dependence of the quantity α/ν^2 in the system AA – H$_2$O – ZnCl$_2$ at the temperature 298.15 K.

Finally, all of dependences indicate that in the system of CHAA – H$_2$O – ZnCl$_2$ two kinds of relaxation processes can be observed:

1. For lower concentrations of ZnCl$_2$ ($0.2 < x_2 < 0.55$), the composition of the complex which takes part in the relaxation results from x_{max1}, where the ratio of molecules is: CHAA : ZnCl$_2$ = 4 : 3. This ratio indicate the composition of the complexes : Zn(H$_2$O)$_2$(CHAA)$_4^{2+}$ + ZnCl$_4^{2-}$ + ZnCl$_2$ which create and disintegrate during the relaxation process with $\tau \cong 11.5$ ns.

2. For higher concentration of ZnCl$_2$ ($0.55 < x_2 < 0.9$), the composition of the complex which takes part in the relaxation results from x_{max2}, where the ratio of molecules is: CHAA : ZnCl$_2$ = 1 : 3. This ratio indicate the composition of the complexes: Zn^{2+}(H$_2$O)$_3$(CHAA)Cl$_2^-$ + ZnCl$_4^{2-}$ + Zn^{2+} which create and disintegrate during the relaxation process with $\tau \cong 23$ ns.

The assumption that zinc has a coordination number equal to 6 has been made.

5. Final conclusions

• The character of the observed relaxational process in the quasi-two-component solutions CHAA – H$_2$O – ZnCl$_2$ depends strongly on the concentration.

• In the range of lower concentrations of ZnCl$_2$, the observed relaxational process is connected with the preferential solvation of zinc by 2-chloroacetamide molecules. It's indicated by the additional investigations of the AA – H$_2$O – ZnCl$_2$ system, Zn coordinates CHAA molecules though Cl atoms.

• In the range of higher concentrations of ZnCl$_2$ the observed relaxational process is connected with the preferential solvation of zinc by 2-chloroacetamide molecules and water. It's indicated by the additional investigations of the AA – H$_2$O – ZnCl$_2$ system, Zn coordinates CHAA molecules as a whole.

• Additional investigations of the CHAA – H$_2$O – ZnBr$_2$ system indicate a lack of participation the chloride atom from the ZnCl$_2$ molecule in the solvation process for the observed relaxation in the mixed three-component solutions.

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