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COMPLEXITY INVESTIGATION IN SOLUTIONS OF $ZnCl_2$ AND LiCl IN WATER USING AN ACOUSTIC METHOD*

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The formation of complex ions brings about in water solutions a destruction of the water structure, thus leading to the formation of a new structure in the solution which is considerably less cohesive than the original water structure.

The investigations performed with zinc chloride and lithium chloride solutions in water indicate that those solutions in which the ratio of zinc atoms to chlorine atoms is near to 1 : 4, i.e. near to the ratio for the formation of $ZnCl_4^{-2}$, have maximum adiabatic compressibility, minimum hydration number and minimum viscosity. Measurements of the absorption coefficient of ultrasonic waves have shown that the process of relaxation of the formation and disintegration of complex ions with a relaxation time of 10^{-8} s exerts a predominating influence on the sound absorption.

1. Introduction

A complicated interaction between ions and molecules in the solvent leads to the formation, in electrolyte solutions, of strictly defined strucural forms. In some cases these forms are precisely defined but sometimes their definition is obtained only by investigating the solution with many methods. We have to deal with such a situation in the case of water solutions of zinc chloride.

The aim of this paper is to present an acoustic method for investigating the complexity of water solutions of zinc chloride.

Zinc ions Zn^{2+} are comparatively small and according to the data of PAULING [1] their crystallographic radius is equal to $0.74 \cdot 10^{-8}$ m and the charge surface density is 3.67. Chlorine ions Cl^- are considerably larger and have a crystallographic radius of $1.81 \cdot 10^{-8}$ m and a charge denisty equal to 0.31.

In order to obtain a surplus of ions in zinc chloride solution lithium chloride is (preferably) introduced into the solution. Lithium ions Li^+ have a crystallographic radius equal to $0.60 \cdot 10^{-8}$ m and a charge surface density of 2.78.

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The first proposal that zinc may have a co-ordination figure of 4 was made by OSWALD and JAGGI [2]. On the basis of x-ray analysis they found that in anhydrous crystals of $ZnCl_2$, zinc co-ordinates four chloride ions in tetrahedral structures.

Supported by the statements of HARRIS and PARTON [4] that in concentrated water solutions of $ZnCl_2$, the transfer number of zinc ions Zn^{2+} is negative, ROBINSON and STOKES [3] have come to the conclusion that zinc occurs in solution mainly in the form of the $ZnCl_4^{2-}$ complex which, being more weakly hydrated, can have a higher mobility than its anti-ion Zn^{2+}.

In investigating the Raman spectrum DELWAULLE et al. [6] have observed in a water solution of $ZnCl_2$ the occurrence of two weak bands at 275 cm^{-1} which they, after HIBBEN [5], ascribe to the molecule $ZnCl_2$, and 307 cm^{-1}. The addition of a surplus of Cl^- ions causes the transformation of this band into a narrower line with a maximum at 282 cm^{-1} which the authors ascribe to the $ZnCl_4^{2-}$ complex. Delwaulle concludes that such complexes also exist in solutions which do not have a surplus of chlorine ions.

KĘCKI [7-10] has investigated the Raman spectrum in methanol solutions of $ZnCl_2$, in which a surplus of chlorine ions was obtained by adding lithium chloride.

In a methanol solution of $ZnCl_2$ the asymmetry of the contour indicates, in addition to $ZnCl_2$, the presence of the $ZnCl_4^{2-}$ complexes. With the molecular ratio of $ZnCl_2$ to LiCl being equal to 1 : 2 and 1 : 4 these contours become symmetrical at a maximum of 282 cm^{-1} which corresponds to the $ZnCl_4^{2-}$ complex.

The occurrence of $ZnCl_4^{2-}$ complexes in water solutions should be also apparent in the behaviour of characteristics as adiabatic compressibility, hydration number, viscosity etc. Such data can be obtained by the use of an acoustic method applicable for the investigation of the solutions under consideration.

2. Method of investigation

The zinc chloride and lithium chloride used for the preparation of solutions were (partly for analysis) dried at a temperature of 120°C for 10 hours. Doubly distilled water was used as a solvent.

The solutions were prepared in such a way that in 6 moles of water 0,6 moles of electrolyte were dissolved, thus the ratio of salt water to water moles was constant and amounted to 1 : 10. Both zinc chloride and lithium chloride were included in 0.6 mole of salt, their relative amounts changing in such a maner that

$$n_1 + n_2 = 0.6, \tag{1}$$

where n_1 is the number of moles of LiCl, and n_2 is the number of moles of $ZnCl_2$. The mutual concentration k expressed as the percentage of LiCl in the total amount of electrolyte moles (0.6) can be written in the form

$$k = \frac{n_1}{n_1 + n_2} 100\%. \tag{2}$$

In the following text the mutual concentration k will define the percentage of LiCl in the total amount of electrolyte moles.

Seventeen solutions with mutual concentrations: 10.0; 20.0; 30.0; 40.0; 50.0; 60.0; 62.5; 65.0; 66.6; 67.5; 70.0; 72.5; 75.0; 80.0; 90.0; 100.0% LiCl were prepared for the investigation. For better understanding it can be said that at a temperature of 25°C a solution with a mutual concentration $k = 100\%$ LiCl has a concentration of 4.97 mole/l and this amounts to a concentration by weight of 19%, while a solution with $k = 0\%$ LiCl has a concentration of 4.58 mole/l (this would be a solution of zinc chloride alone) and this amounts to a concentration by weight of 43%.

Ultrasonic waves propagate in a liquid medium at a phase velocity defined by the expression

$$c = \sqrt{\frac{1}{\varrho \beta_s}}, \tag{3}$$

where c denotes the propagation velocity of the ultrasonic waves, ϱ is the density of medium, and $\beta_s = -1/v((\partial v/\partial p)_s)$ is adiabatic compressibility.

Knowledge of the propagation velocity of ultrasound and of the solution density permits evaluation of the coefficient of adiabatic compressibility.

$$\beta_s = \frac{1}{\varrho c^2}. \tag{4}$$

This is the only method for simply evaluating the quantity β_s.

Measurements of the propagation velocity of ultrasonic waves at a frequency of 1 MHz were made with the aid of a pulse-phase interferometer type U-13 which permitted measurement of the phase velocity with a relative error (precision) less than 10^{-3}.

The solution density was determined by the specific gravity bottle method with a relative error not exceeding $2 \cdot 10^{-5}$.

If the adiabatic compressibilities of the solution and the pure solvent are denoted by β_s and β_{s_0} respectively and the incompressible part of the solvent in the solution [11] by X, one can write

$$V\beta_s = n_1 V'_0 \beta_{s_0}(1-X), \tag{5}$$

where n_1 denotes the total number of moles of the solvent in the solution, V_0 is the mean molar volume of pure solvent, and V is the volume of solution. As a result it is possible to evaluate the hydration number from the expression

$$Z = \frac{n_1}{n_2}\left(1 - \frac{V\beta_s}{n_1 V'_0 \beta_{s_0}}\right), \tag{6}$$

where n_2 is the number of moles of the dissolved electrolyte.

While propagating in a medium the ultrasonic wave loses some of its energy in dissipative processess. The displacement of a particle of the medium due to the propagating ultrasonic wave is described by the expression

$$u = Ae^{-\alpha x}\, e^{i(\omega t - kx)}, \tag{7}$$

where α — denotes the absorption coefficient of the ultrasonic wave.

Stokes and Kirchhoff, from consideration of the viscosity and thermal conductivity losses have derived a formula for the absorption coefficient of ultrasonic waves [12]

$$\alpha = \frac{2\pi^2 f^2}{\varrho c^3}\left(\frac{4}{3}\eta + \frac{C_p/C_v - 1}{C_p} K\right), \tag{8}$$

where η denotes the coefficient of dynamic viscosity, C_p is the specific heat at constant pressure, C_v is the specific heat at constant volume, ϱ is the density of medium, f is the frequency of the ultrasonic wave, c is the velocity of propagation of the ultrasonic wave, and K is the coefficient of thermal conductivity.

It follows from this formula that

$$\frac{\alpha}{f^2} = \text{const}. \tag{9}$$

If molecular processes induced by the ultrasonic wave occur in a medium, then the dependence of α/f^2 on the frequency takes another form, as becomes apparent in the graph of the dependence of $\alpha\lambda$ on the frequency.

A point of inflexion on the curve α/f^2 and a maximum on the curve $\alpha\lambda$ can be used to determine the frequency of a relaxation process.
Hence, it is easy to determine the relaxation time

$$\tau = \frac{1}{2\pi f r}. \tag{10}$$

The absorption coefficients of ultrasonic waves at frequencies of 9.8; 13.3; 16.6; 20.0; 30.0; 42.0; 50.0 MHz were measured by means of a high-frequency ultrasonic unit US 4/6 with a maximum relative error in the determination of the absorption coefficient of 9 % at 9.8 MHz and 1 % at 50 MHz.

The dynamic viscosity of the solutions examined was determined from measurements made using a Höppler viscosimeter type BH-2 with a relative error not exceeeding 0.15 %. The konwledge of the viscosity coefficient permitted comparison of the calculated classical coefficient of the absorption of ultrasonic waves with the values actually measured. In these investigations the measuring vessels were thermostaticaly controlled; the temperature was measured with the aid of a thermistor type OTP-11 with a nominal resistance of 100 Ω, operating in a Wheatsone bridge circuit. The temperature was measured to an accuracy of 0.1 deg. It is also worth noting that all the measurements were performed in perfectly sealed measuring vessels, thus preventing a change in the concentration of the examined solutions as a result of water evaporating.

3. Results of the investigations

The measurements of the velocity of propagation of ultrasonic waves in the seventeen solutions examined were performed at five temperatures: 25, 30, 35, 40 and 45° C. Fig. 1 shows the dependence of the sound velocity on the temperature.

Concurrently with the measurements of the sound velocity the density of the liquids was also measured. The measured values of the density are shown as a function of the temperature in Fig. 2.

Knowledge of the velocity of propagation of ultrasonic waves and of the density of the liquids permits calculation of the coefficient of adiabatic compressibility. The results of these calculations are presented in Fig. 3.

On the basis of the results obtained for the coefficients of adiabatic compressibility of the solutions, the hydration numbers were evaluated from formula (6). Fig. 4 shows the relationship between the hydration number and the mutual concentration of water solutions of $ZnCl_2$ and LiCl.

The dependence of the measured values of the coefficient of dynamic viscosity of the liquids on the mutual concentration is shown in Fig. 5.

The classical theory of Stokes and Kirchhoff on the loss of energy of an ultrasonic wave as a result of viscosity and thermal conductivity in a medium makes it possible to calculate the absorption coefficient of ultrasonic waves according to the equation (8). The results of these calculations in the form of the dependence of α/f^2 on the frequency for various mutual concentrations of solutions are shown in Fig. 6.

The measured values of the absorption coefficient of ultrasonic waves in the solutions examined differ from the values calculated according to classical theory. Figs. 7 and 8 present the results of measurements of the absorption coefficient of sound in the form of the dependencies of α/f^2 and $\alpha\lambda$ on the frequency of ultrasonic waves.

4. Analysis and discussion of the results of the investigations

From previous investigations of solutions of zinc chloride it followed that zinc chloride exists in water and methanol solutions mainly in the form of $ZnCl_4^{2-}$. If one introduces a surplus of chloride ions into the water solution of zinc chloride by dissolving lithium chloride, then by changing the amount of lithium chloride it is possible to change the ratio of zinc atoms to chlorine atoms in the solution. The method of preparing the solution selected for these

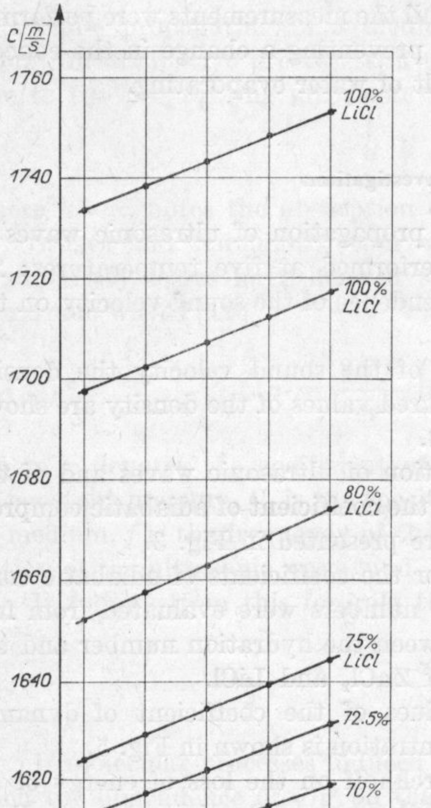

Fig. 1. The dependence of the velocity of propagation of ultrasonic waves on the temperature in water solutions of $ZnCl_2$ and LiCl, for various concentrations

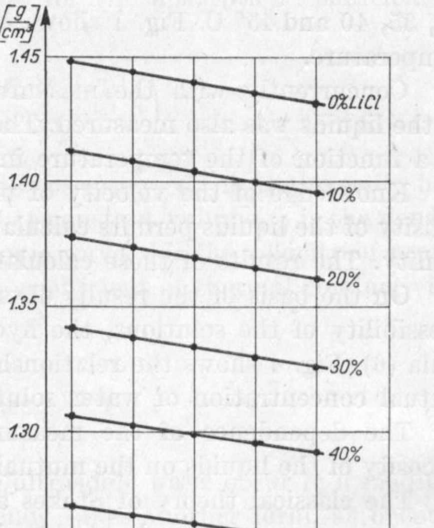

Fig. 2. The dependence of the density of water solutions of $ZnCl_2$ and LiCl on the temperature, for various mutual concentrations

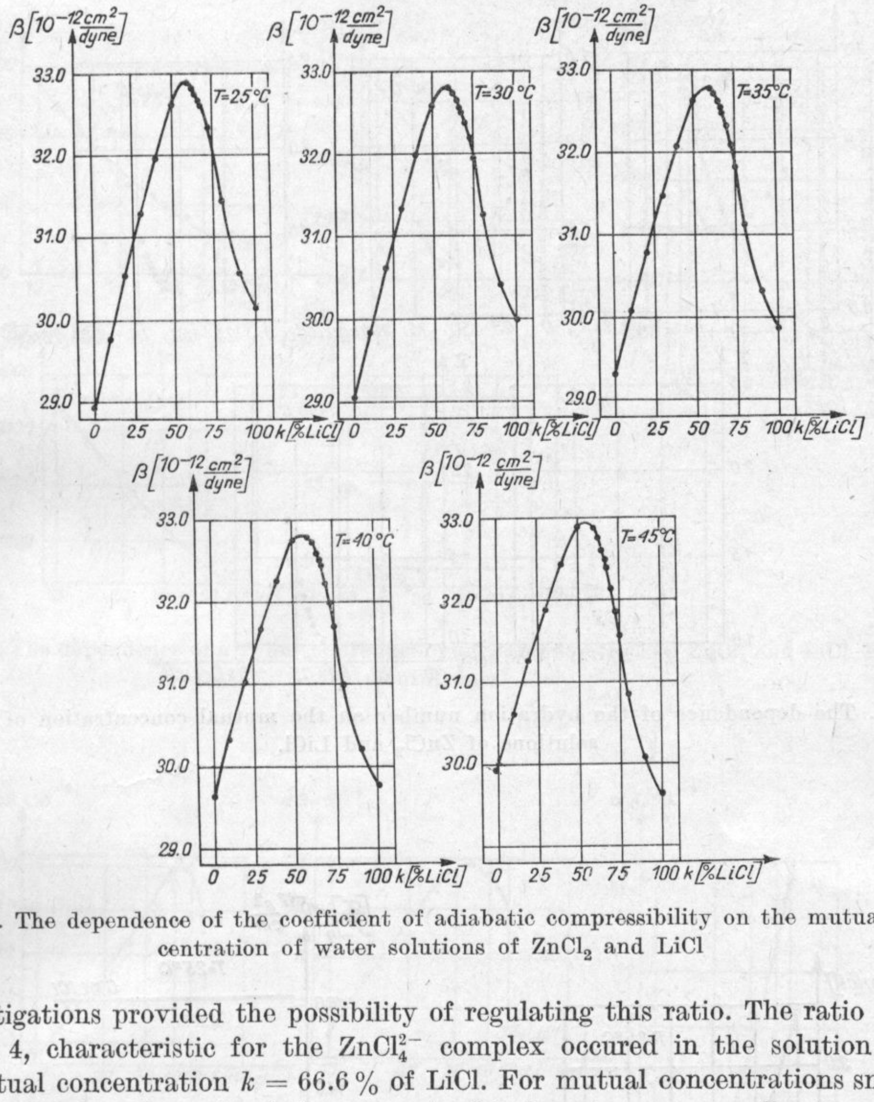

Fig. 3. The dependence of the coefficient of adiabatic compressibility on the mutual concentration of water solutions of $ZnCl_2$ and LiCl

investigations provided the possibility of regulating this ratio. The ratio equal to 1 : 4, characteristic for the $ZnCl_4^{2-}$ complex occured in the solution with a mutual concentration $k = 66.6\,\%$ of LiCl. For mutual concentrations smaller than this value, the ratio of zinc atoms to chlorine atoms was smaller than 1 : 4; for higher concentrations the ratio was greater.

The dependence of the velocity of propagation of ultrasonic waves in water on the temperature is parabolic, being described by the expression given by Willard [14],

$$c = 1557 - 0.0245(74 - t)^2 \text{ m/s}, \tag{15}$$

with a maximum at a temperature of 74 °C. Dissolving electrolyte in the water causes a shift in the position of the maximum of the sound velocity towards smaller temperatures.

It follows from Fig. 1 that a solution of pure zinc chloride with a mutual

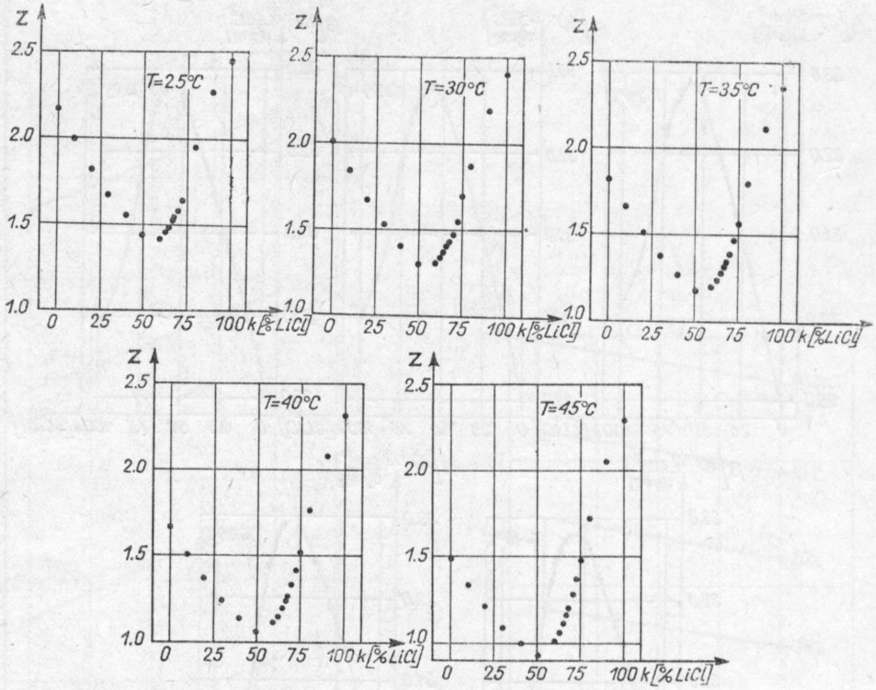

Fig. 4. The dependence of the hydration number on the mutual concentration of water solutions of $ZnCl_2$ and LiCl.

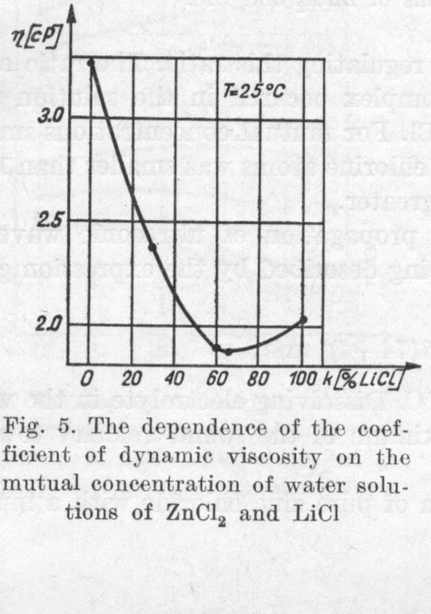

Fig. 5. The dependence of the coefficient of dynamic viscosity on the mutual concentration of water solutions of $ZnCl_2$ and LiCl

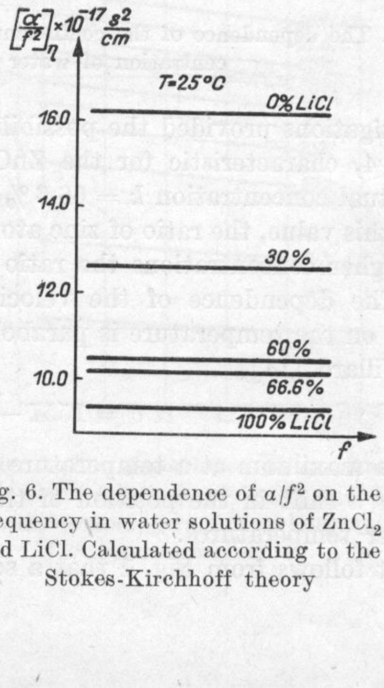

Fig. 6. The dependence of α/f^2 on the frequency in water solutions of $ZnCl_2$ and LiCl. Calculated according to the Stokes-Kirchhoff theory

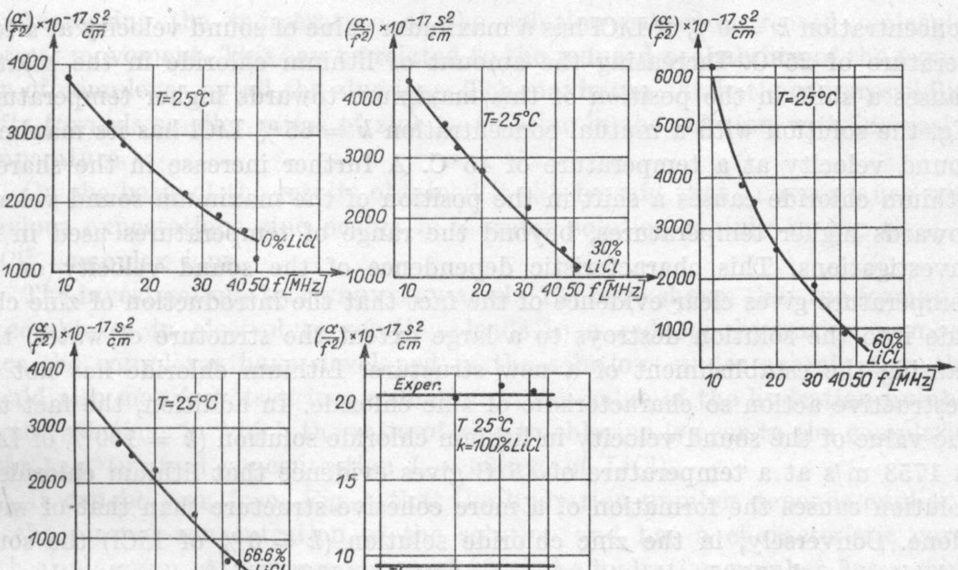

Fig. 7. The dependence of α/f^2 on the frequency in water solutions of $ZnCl_2$ and LiCl. Experimental data

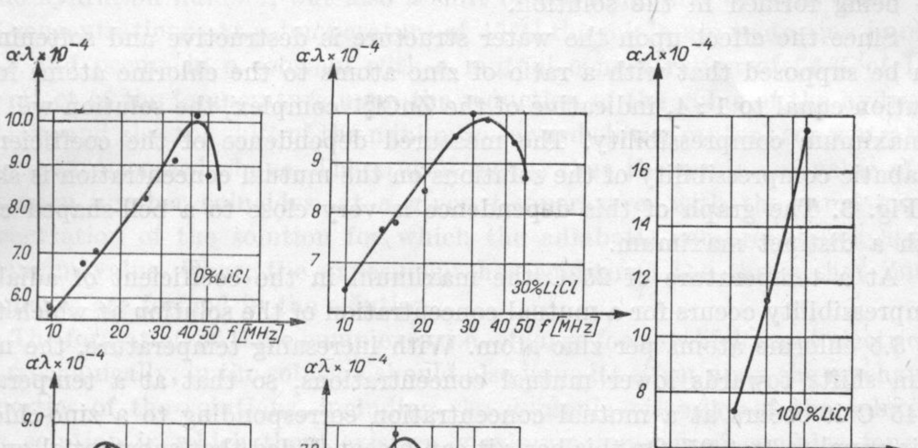

Fig. 8. The dependence of $\alpha\lambda$ on the frequency in water solutions of $ZnCl_2$ and LiCl. Experimental data

concentration $k = 0\%$ of LiCl has a maximum value of sound velocity at a temperature of 25°C. Increasing the amount of lithium chloride in the solution causes a shift in the position of this maximum towards higher temperatures, e.g. the solution with a mutual concentration $k = 65\%$ LiCl has its maximum sound velocity at a temperature of 45°C. A further increase in the share of lithium chloride causes a shift in the position of the maximum sound velocity towards higher temperatures, beyond the range of temperatures used in the investigations. This characteristic dependence of the sound velocity on the temperature gives clear evidence of the fact that the introduction of zinc chloride into the solution destroys to a large extent the structure of water, thus causing the establishment of a new structure. Lithium chloride has not the destructive action so characteristic of zinc chloride. In addition, the fact that the value of the sound velocity in lithium chloride solution ($k = 100\%$ of LiCl) is 1753 m/s at a temperature of 45°C gives evidence that lithium chloride in solution causes the formation of a more cohesive structure than that of water alone. Conversely, in the zinc chloride solution ($k = 0\%$ of LiCl) the sound velocity equals 1527 m/s at a temperature of 45°C. This is smaller than the value in water alone, thus confirming the destructive action of zinc chloride upon the water structure. Such a situation suggests that large complex ions develop in the solution and it is zinc that mainly accounts for this.

On the basis of previous data it might be expected that $ZnCl_4^{2-}$ complexes are being formed in the solution.

Since the effect upon the water structure is destructive and softening, it can be supposed that with a ratio of zinc atoms to the chlorine atoms in the solution equal to 1 : 4, indicative of the $ZnCl_4^{2-}$ complex, the solution will have a maximum compressibility. The measured dependence of the coefficient of adiabatic compressibility of the solutions on the mutual concentration is shown in Fig. 3. The graph of this dependence is very close to a bell-shaped curve with a distinct maximum.

At a temperature of 25°C the maximum in the coefficient of adiabatic compressibility occurs for a mutual concentration of the solution at which there are 3.5 chlorine atoms per zinc atom. With incresaing temperature, the maximum shifts towards lower mutual concentrations, so that at a temperature of 45°C it occurs at a mutual concentration corresponding to a zinc-chloride ratio equal to 1 : 3.25. On this basis it can be concluded that substantial quantities of $ZnCl_4^{2-}$ complexes develop in the solutions under consideration, and that these complexes exert a strong influence upon the adiabatic compressibility of the solution. If one takes into consideration the fact that the probability of all the zinc ions in the solution forming complex ions is very low, it is not surprising that experimentally we find a maximum in the adiabatic compressibility in solutions in which the ratio of the number of zinc atoms to the number of chlorine atoms is some-what smaller than the complexity ratio 1 : 4. Some of the ions will be bonded in ion pairs of the form $Zn^{2+} \cdot ZnCl_4^{2-}$.

Increasing the temperature of the solution causes increased molecular thermal movement. This can be related to the reduced probability of the formation of complexes by all the zinc ions. The maximum adiabatic compressibility shifts towards smaller ratios of zinc to chlorine in the solution with increasing temperature.

On the basis of the results obtained it can be said that in accordance with previous expectations zinc occurs in a water solution mainly in the form of $ZnCl_4^{2-}$ complex ions.

The investigations by Surovtzev at al. [15] have shown that the formation of complexes in electrolyte solutions leads to a reduced hydration number. Once the complexes have developed in the solutions under examination this should also manifest itself in a reduction in the value of the hydration number for the solutions in which the ratio of zinc to chlorine is near to the complesity ratio 1 : 4 (mutual concentration $k = 66.6\ \%$ of LiCl).

It can be seen from Fig. 4 that the hydration number depends explicitly on the mutual concentration of the solution and has a characteristic curve with a minimum. At a temperature of 25°C the hydration number has a minimum value, equal to 1.42, in the solution in which the ratio of zinc to chlorine is equal to 1 : 3.5 and in the same solution for which there occurs, at this temperature, a maximum in the coefficient of adiabatic compressibility. An increase in the temperature causes not only a reduction of the minimum value of the hydration number, but also a shift of the minimum towards lower mutual concentrations. At a temperature of 45°C the minimum hydration number is 0,9 and occurs in a solution with a mutual concentration of 52 % of LiCl. The effect of the temperature upon the reduction of the value of the hydration number, and also the shift of the minimum towards lower mutual concentrations have been discussed above. The crucial fact is that the minimum value of the hydration number coincides, at a given temperature, with the same mutual concentration of the solution for which the adiabatic compressibility has its maximum value. Thus, the experiment has confirmed the thesis that $ZnCl_4^{-2}$ complexes are formed in the solution.

The formation of these complexes, i.e. of large forms which react electrically and mechanically, in the solution should also have its effect upon the mechanical properties of the solutions, including the dynamic viscosity of the solutions. In a solution in which there exists a maximum number of complex ions the dynamic viscosity should possess a minimum value because of the reduction of liquid cohesion by the complexes. The dependence of the dynamic viscosity of the solutions on the mutual concentration is shown in Fig. 8. The minimum dynamic viscosity (1.887 cP) is exhibited by the solution with a mutual concentration of $k = 66.6\ \%$ of LiCl, and this corresponds to the complexity ratio of zinc to chlorine. This is another experimental fact which supports the conception that zinc in water solutions occurs chiefly in the form of $ZnCl_4^{2-}$ complexes.

It seems to be very interesting that the viscosity coefficient of the zinc chloride solution ($k = 0\,\%$ of LiCl) is 3.280 cP while the viscosity coefficient of the lithium chloride solution ($k = 100\,\%$ of LiCl) has a considerably smaller value equal to 2.045 cP. In addition, the increase in the number of chlorine ions in the solution causes a reduction of the viscosity of the solution, as a result of the formation of an ever greater number of $ZnCl_4^{2-}$ complexes. It seems to support the hypothesis stated by Kęcki [10] that zinc chloride also exists in the solution in the form of $ZnCl_2$"polymers", the occurrence of which involves a high viscosity for the solution.

The measurements made of the absorption coefficient of ultrasonic waves in the solutions examined also provide much valuable information. The quantity α/f^2 has a value independent of the frequency of the ultrasonic waves only for the lithium chloride solution, $k = 100\,\%$ of LiCl, although the experimentally determined value is more than twice as high as the value calculated from the Stokes-Kirchhoff formula. For all the solutions containing zinc chloride the dependence of α/f^2 on the frequency has a character which gives evidence of the effect of the molecular relaxation process on she sound absorption in the liquids examined. This effect can be seen distinctly when one considers the dependence of the sound absorption times the wavelength $\alpha\lambda$ and its relationship to the frequency of the ultrasonic waves. The graphs of this dependence represent relaxation sound absorption in the solutions examined. On the basis of both dependencies it is possible to estimate the time of the relaxation process: which attains its maximum value of $1 \cdot 10^{-8}$ s for the solution with a mutual concentration of $k = 60\,\%$ od LiCl (Zn : Cl = 1 : 3.5). It seems most warranted to associate the relaxation process discovered with the formation and disintegration of complex $ZnCl_4^{2-}$ ions. This suggestion seems to be confirmed by the fact that the longest time for the relaxation process is found for solutions with a mutual concentration of $k = 60\,\%$ of LiCl in which optimal conditions are created for the formation of complex ions, and this in turn effects a high stability for the structure of the solution.

5. Summing up and conclusions

The acoustic method used in the investigations seems to be a good method for the verification of the previous hypotheses and suggestions as to the form in which zinc chloride occurs in water solutions.

The results obtained show clearly that zinc chloride occurs in water solutions chiefly in the form of complex $ZnCl_4^{2-}$ ions. The solutions in which the ratio of the number of zinc ions to the number of chlorine ions is some-what smaller than the ratio required for the formation of the complex $ZnCl_4^{2-}$, are characterized by a maximum adiabatic compressibility, a minimum hydration number, and a minimum dynamic viscosity; while the relaxation process of the formation and disintegration of the complexes has a decisive effect on the absorption of ultrasonic waves in the solutions. The time of this relaxation process is estimated on the basis of the analysis of the sound absorption, at 10^{-8} s.

The results of the investigations carried out do not indicate that $ZnCl_3^-$ complexes are formed in water solutions of zinc chloride. Should such complexes exist in large quantities, then this would have influenced the adiabatic compressibility of the solutions and the values of the hydration number in those solutions in which the ratio of the number of zinc atoms to the number of chlorine atoms would be equal to or somewhat smaller than the ratio 1 : 3

The proven fact of the diminishing dynamic viscosity of the solution with an increasing number of chlorine atoms in the solution gives evidence for the validity of the hypothesis stated by Kęcki that zinc chloride also occurs in the solution in the form of $(ZnCl_2)_n$"polymers". The increase in the amount of chlorine in the solution must cause an increase in the number of complex $ZnCl_4^{2-}$ ions, thus reducing the chain numbers of the "polymers" and thus causing the viscosity to decrease.

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