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ABSORPTION OF ULTRASONIC WAVES IN $ZnCl_2$ SOLUTIONS IN METHANOL

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The investigation of the absorption of ultrasonic waves in $ZnCl_2$ solutions in methanol has shown the occurrence of a relaxation process which is considered, in this paper, to be the disintegration and the formation of ion pairs. The activation energy has been determined on the basis of the temperature dependence of the relaxation time of this process, while reaction rate constants have been established from the concentration dependence of the relaxation time. In the solutions investigated a concentration of 2.0 mol/l is a characteristic concentration, above which the structure of the solution becomes considerably stabilized.

1. Introduction

Zinc chloride solutions in methanol has a number of interesting physical properties which distinguish them from other electrolyte solutions. Results obtained hitherto indicate that zinc chloride occurs in the methanol solution in configurations determined by a series of equilibriums:

$$Zn^{2+} + 2\,Cl^- \rightleftharpoons ZnCl_2, \tag{1}$$

$$2\,ZnCl_2 \rightleftharpoons Zn^{2+} + ZnCl_4^{2-}, \tag{2}$$

$$n\,ZnCl_4^{2-} + n\,Zn^{2+} \rightleftharpoons 2n\,ZnCl_2 \rightleftharpoons (ZnCl_2)_{2n}. \tag{3}$$

$ZnCl_2$ can also occur in the form of tetra and octahedral complexes which coordinate methanol molecules as ligands. The equilibrium described by equation (1) occurs in solutions with very small concentrations ($k < 0.1$ mol/l). In solutions with higher concentrations the predominate configurations are described by equations (2) and (3). Investigations of Raman spectra have shown that zinc chloride molecules in a methanol solution combine into "polymer" chains in which the number of molecules varies within broad limits. However, Zn^{2+} ions and $ZnCl_4^{2-}$ complex ions cannot exist only in the form of free ions since the Bjerrums critical distance for the formation of ion pairs is exceeded throughout the whole volume of the solution at concentrations above 0.11 mol/l at a temperature of 25° C. Thus in addition to equations (1) to (3), the equation describing the equilibrium of the decomposition and formation of ion pairs should also be considered:

$$Zn^{2+} \times ZnCl_4^{2-} \rightleftharpoons Zn^{2+} + ZnCl_4^{2-}. \tag{4}$$

The investigation of the absorption of ultrasonic waves in solutions can supply a valuable information on the kinetics of the reaction and activation energy of processes encountered.

It follows from classical Stokes-Kirchhoff theory that the absorption coefficient of ultrasonic waves in a liquid is proportional to the square of the wave frequency, the medium viscosity and the thermal conductivity. Hence, the important conclusion can be drawn that in a liquid in which relaxation processes do not occur, the ratio of the coefficient of sound absorption to the square of the frequency is constant, i.e.

$$\frac{a_{\text{classical}}}{f^2} = \text{const}. \tag{5}$$

When a relaxation process occurs in a liquid, relation (5) is not satisfied and must take the form

$$\frac{a}{f^2} = \frac{A}{1+(f/f_r)^2} + B, \tag{6}$$

where f_r denotes a relaxation frequency, and A and B are constants.

The constant A involves an information about the contribution of the relaxation process to the absorption, whereas the constant B describes the

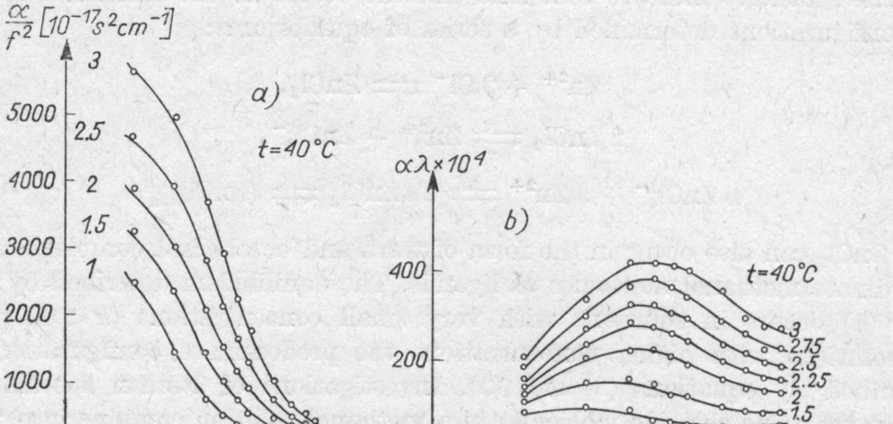

Fig. 1. a/f^2 and $a\lambda$ as functions of frequency in solution of $ZnCl_2$ in methanol; $t = 40°C$

absorption of ultrasonic waves caused by the viscosity, heat conductivity, and relaxation processes whose relaxation times are considerably shorter than the relaxation time of the process under consideration.

It is a good practice to consider the measurement results of the absorption of ultrasonic waves in the forms of the relation α/f^2 versus frequency (for $f = f_r$ there is a turning point in the graph) and the relationship $\alpha\lambda$ versus frequency (for $f = f_r$ the graph has a maximum).

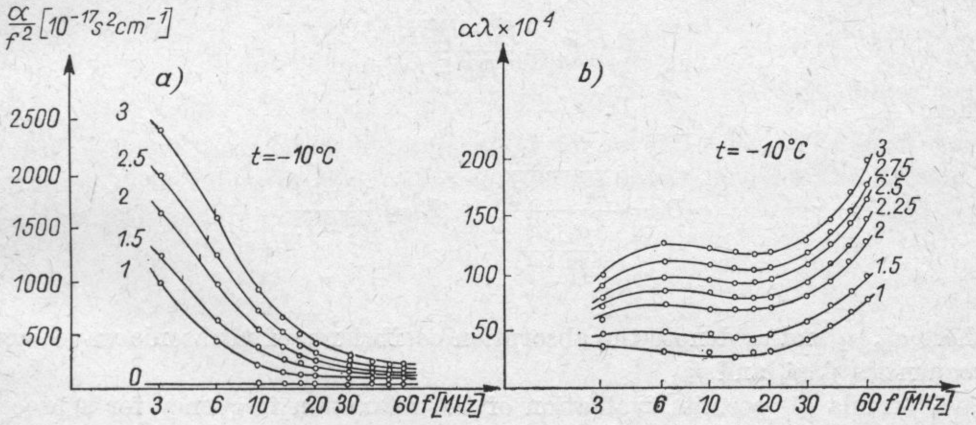

Fig. 2. α/f^2 and $\alpha\lambda$ as functions of frequency in solution of $ZnCl_2$ in methanol; $t = -10°C$

2. Method and experimental results

The solutions investigated were prepared with the concentration ranging from 0.1 to 3.0 mol/l using carefully dehydrated methanol and zinc chloride. The maximum error of the concentration determination was 75×10^{-4} mol/l.

The measurements of the absorption coefficient of ultrasonic waves in the solutions were made using an ultrasonic pulse-phase interferometer UI-13 and a high-frequency ultrasonic unit US-4 (maker: IPPT PAN, Warsaw) in the frequency range from 3 MHz to 60 MHz. The relative error of the determination of the absorption coefficient of ultrasonic waves varies from 6 % for $f = 3$ MHz to 1 % for $f = 60$ MHz.

The systems used for thermostatic control and temperature measurement permit the determination of the temperature of the investigated solution to an accuracy of ±0.1 deg.

The measuring vessels together with probes were carefully sealed in order to prevent evaporation of the solvent and consequent changes in the concentration of the investigated solutions.

The results of measurements of the absorption coefficient of ultrasonic waves were analyzed as α/f^2 and $\alpha\lambda$ as functions of frequency. From this analysis it can be concluded that within the range of ultrasonic waves, concentrations and temperatures used molecular relaxation processes are seen to contribute to the sound absorption.

To determine exactly the relaxation frequency, the advantage has been taken of the following method. The relation α/f^2 versus frequency can be presented by formula (6).

Since an exact determination of the constants A and B has been impossible within the applied frequency range, equation (6) is transformed to take the form

$$f_r^2 = \frac{f_3^2 - DEf_2^2}{DE-1}, \tag{7}$$

where

$$D = \frac{\frac{\alpha_1}{f_1^2} - \frac{\alpha_2}{f_2^2}}{\frac{\alpha_1}{f_1^2} \frac{\alpha_3^2}{f_3^2}}, \qquad E = \frac{f_3^2 - f_1^2}{f_2^2 - f_1^2},$$

where α_1, α_2 and α_3 denote the absorption coefficients of ultrasonic waves with frequencies f_1, f_2 and f_3.

Formula (7) permits evaluation of the relaxation frequency for a process with a discrete time of relaxation on the basis of the three values of α/f^2 determined experimentally.

For the temperatures and concentrations established ten measurements of α/f^2 at ten frequencies were made. The number of combinations without the repetition of 10 elements – 3 elements each – equals 120. The total number of 120 three-element combinations has been reduced to 56 by the elimination of combinations containing the measurement points for neighbouring measurement frequencies, i.e. only the threes of non-neighbouring measurement points have been considered. The relaxation frequency for each of three-element combinations of values of α/f^2 was evaluated, and the obtained results averaged to obtain the value of the relaxation frequency $\bar{f}_r$. For this value of $\bar{f}_r$, relations using the measurement points were plotted againts frequency. The results of this analysis are presented for several selected temperatures and solution concentrations in Figs. 1 and 2 in the forms of α/f^2 and $\alpha\lambda$ against frequency.

3. Analysis of experimental results

The relaxation frequencies determined in the investigations increase with increasing temperature and solution concentration. One such relation indicates that the detected relaxation process is a thermally activated process of chemical relaxation.

The time of relaxation of a thermally activated process obeys Arrhenius' law

$$\tau = \tau_0 \exp\frac{E}{RT}, \tag{8}$$

where E denotes the activation energy of the process, R is the gas constant, T – the absolute temperature, and τ_0 – a constant.

The activation energy of the process can be determined from the slope of the straight line representing the relation $\ln\tau$ versus $1/T$, resulting from the relation

$$\ln\tau = \ln\tau_0 + \frac{E}{RT} = \text{const} + \frac{E}{R}\frac{1}{T}. \tag{9}$$

Fig. 3 shows the relation $\ln\tau$ versus $1/T$ for several selected solution concentrations. The values of the activation energy, determined for the detected relaxation process, are given in Table 1.

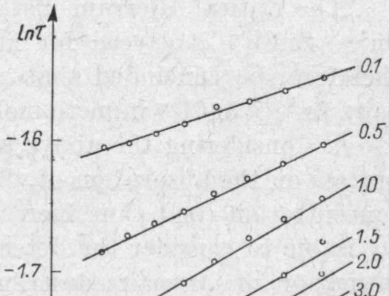

Fig. 3. $\ln\tau$ versus T^{-1} for several selected solution concentrations of $ZnCl_2$ in methanol

Previous investigations of solutions of zinc chloride in methanol [3, 7-10] indicate that zinc chloride occurs in the solution primarily in the form of complex ions $ZnCl_4^{2-}$ and zinc ions Zn^{2+}. The zinc ion is distinguished by a very large surface density of electric charge and a small radius ($r = 0.74$ Å). These imply its strong interaction with the molecules of the solvent and other ions in the solution. $ZnCl_4^{2-}$ complexes are large and their surface charge density is considerably smaller than that of Zn^{2+} ions and they exhibit very great longevity.

Table 1. Values of the activation energy E and its dependence on the solution concentration

$k\left[\frac{\mathrm{mol}}{\mathrm{l}}\right]$	0.10	0.20	0.30	0.40	0.50	0.60
$E\left[\frac{\mathrm{kcal}}{\mathrm{mol}}\right]$	1.15	1.45	1.68	1.86	1.99	2.06
$k\left[\frac{\mathrm{mol}}{\mathrm{l}}\right]$	0.70	0.80	1.00	1.25	1.50	1.75
$E\left[\frac{\mathrm{kcal}}{\mathrm{mol}}\right]$	2.12	2.17	2.24	2.32	2.38	2.43
$k\left[\frac{\mathrm{mol}}{\mathrm{l}}\right]$	2.00	2.25	2.50	2.75	3.00	
$E\left[\frac{\mathrm{kcal}}{\mathrm{mol}}\right]$	2.47	2.49	2.50	2.51	2.52	

The critical Bjerrum distance for the formation of ion pairs of the type $\mathrm{Zn}^{2+}\times\mathrm{ZnCl}_4^{2-}$ is exceed for nearly all of the solutions investigated. It can, therefore, be concluded that zinc chloride occurs mainly in the form of ion pairs $\mathrm{Zn}^{2+}\times\mathrm{ZnCl}_4^{2-}$ in methanol solutions of the range of concentrations investigated. Considering the above and the fact that the influence of the relaxation process on the absorption of ultrasonic waves increases with increasing solution concentration (and thus increasing concentration of ion pairs), it seems most advisable to consider the detected relaxation process as the disintegration and formation of ion pairs described by the equilibrium

$$\mathrm{Zn}^{2+}\times\mathrm{ZnCl}_4^{2-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{Zn}^{2+}+\mathrm{ZnCl}_4^{2-},$$

(1) (2)

where k_{12} and k_{21} denote reaction rate constants, condition (1) denoting the ion pair and condition (2) free ions.

In view of the lack of data for the dissociation constant, the activity coefficients and other quantities describing the solution, the relation between the relaxation time and the solution concentration can be presented in the form

$$\frac{1}{\tau} = k'_{12} + k'_{21}\,k, \tag{10}$$

where k'_{12} and k'_{21} denote apparent reaction rate constants, k is the solution concentration and τ — the relaxation time.

The relaxation time is related to the relaxation frequency by the simple relation

$$f_r = \frac{1}{2\pi\tau}. \tag{11}$$

The apparent reaction rate constants can thus be determined from a graph presenting the relation between the relaxation frequency and the solution concentration. This relation is presented for three selected temperatures in Fig. 4. It is possible to distinguish two concentration ranges for which the reaction rate constants differ considerably: low concentrations, ranging from 0.1 to about 2.0 mol/l, and high concentrations, ranging from 2.0 to 3.0 mol/l. The value of the apparent reaction rates for two concentration ranges are given in Table 2.

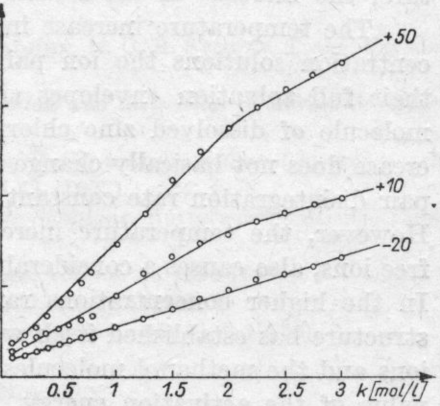

Fig. 4. Relaxation frequency as a function of solution concentration for $ZnCl_2$ in methanol

Table 2. Apparent constant reaction rates as a function of temperature

t [°C]	Lower concentration range		Higher concentration range	
	k'_{12} [$10^6\,\mathrm{s}^{-1}$]	$k'_{21}\left[10^6\,\frac{1}{\mathrm{mol\,s}}\right]$	k'_{12} [$10^6\,\mathrm{s}^{-1}$]	$k'_{21}\left[10^6\,\frac{1}{\mathrm{mol\,s}}\right]$
−20	5.0	9.4	5.0	9.4
−10	5.0	12.5	13.2	9.8
0	5.0	14.4	18.8	11.7
10	5.0	18.2	19.7	12.1
20	5.0	21.0	20.1	13.2
30	5.0	24.8	22.0	16.6
40	5.0	28.2	30.1	18.0
50	5.0	32.3	31.4	19.2

The increased solution concentration causes increased interaction between the ions and the molecules of the solvent. The concentration of about 2.0 mol/l is a characteristic solution concentration for zinc chloride in methanol. As the concentration increases to reach this value, the activation energy of the process increases quite rapidly, but changes insignificantly with further increase of the concentration above this value. In the lower concentration range, the disintegration rate constant of ion pairs is independent of the temperature, while the recombination rate constant of ion pairs increases with increasing temperature. In the higher concentration range both the disintegration rate constant and the recombination rate constant increase with increasing solution temperature, the increase of the former being greater.

The temperature increase increases the mobility of free ions. In low concentration solutions the ion pair disintegrates into ions which easily obtain their full solvation envelopes since the number of methanol molecules per molecule of dissolved zinc chloride is sufficiently large. The temperature increase does not basically change this situation in the solution and thus the ion pair disintegration rate constant has a value independent of the temperature. However, the temperature increase, while causing increased mobility of the free ions, also causes a considerable increase of the recombination rate constant. In the higher concentrations range, above 2.0 mol/l, a fairly stable solution structure has established itself as a result of increased interaction between the ions and the methanol molecules. This finds its expression in a little changing value of the activation energy. A strong interaction and structural stability imply that, as the temperature increases, the rate of the establishment of a new equilibrium in the solution increases, bringing about an increase in the disintegration rate constant and in the formation of ion pairs in the solution.

4. Conclusions

Investigations of the absorption of ultrasonic waves in methanol solutions of zinc chloride have shown the considerable effect of a molecular relaxation process on the sound absorption. On the basis of the results of other methods of investigating these solutions, it can be concluded that one such process is that of the disintegration and formation of ion pairs, the components of which are zinc ions Zn^{2+} and complex ions $ZnCl_4^{2-}$, described by the equilibrium

$$Zn^{2+} \times ZnCl_4^{2-} \rightleftharpoons Zn^{2+} + ZnCl_4^{2-}.$$

The activation energy of this process increases considerably as the solution concentration increases from 0.1 to about 2.0 mol/l, increasing insignificantly with further concentration increase. At a concentration of about 2.0 mol/l there also occur changes in the value and the tendency to increase of the reaction rate constant. It can be concluded that the structure of methanol solutions of $ZnCl_2$ undergoes considerable stabilization above a concentration of 2.0 mol/l.

The temperature dependence of the relaxation time is strong evidence that the said process is activated thermally. The high absorption of ultrasonic waves, resulting from this process, suggests that it is primarily caused by ion pairs in the solution.

References

[1] K. Tamm, *Proceedings of the International School of Physics «Enrico Fermi»*, Academic Press, New York, London 1963.

[2] J. Stuehr, E. Yeager, *Physical Acoustics*, Edited by Warren P. Mason, Academic Press, New York, London 1965, Volume II, Part A.

[3] *Spectral investigations of the structure of electrolyte solution*, Collective work [in Polish], PWN, Warszawa 1969.

[4] M. J. Blandamer, D. E. Clarke, N. J. Hidden, M. C. R. Symons, Trans. Faraday Soc., **64**, 1193 (1968).

[5] K. F. Herzfeld, T. A. Litovitz, *Absorption and dispersion of ultrasonic waves*, Academic Press, New York, London 1959.

[6] W. Boch, *Investigations of the solvation of $ZnCl_2$ ions in methanol by an acoustic method* [in Polish], Archiwum Akustyki, **12**, 1, 25-33 (1977).

[7] R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Butterworths Science Publications, London 1959.

[8] M. L. Delwaulle, Bull. Soc. Chim. France, volume no 1294 (1955).

[9] H. R. Oswald, H. Jaggi, Helv. Chim. Acta, **43**, 72 (1960).

[10] A. C. Harris, H. N. Parton, Trans. Faraday Soc., **36**, 1139 (1940).

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