

ACOUSTICAL STUDIES OF THE SOLVATION OF $ZnCl_2$ IN METHANOL SOLUTIONS

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Measurements of the ultrasonic velocity at 15 MHz and the density of $ZnCl_2$ solutions in methanol permitted determination of the dependence of the adiabatic compressibility of the solutions on temperature and concentration. The independence of the evaluated solvation numbers from the temperature and the insignificant decrease of their values with increasing solution concentration give evidence of the establishment in the solution of stable solvation complexes bound with complex ions $ZnCl_4^{2-}$.

1. Introduction

Electrolyte solutions are investigated by various physical methods including an acoustical technique. At the root of the acoustical method lies the unbalancing of the local thermodynamical equilibrium of the tested medium by the propagation of an acoustic wave.

Hydrous electrolyte solutions have been thoroughly investigated by the acoustical method and a great many papers [1] have been written on the subject. However, on the subject of electrolyte solutions in organic solvents there are only few papers available [2-7]. The aim of the work described in this paper is the determination of the effect of dissolved zinc chloride on the compressibility of methanol solutions and the evaluation of solvation numbers.

Methanol is a liquid strongly associated by hydrogen bonds. It can be generally assumed that methanol molecules may occur in the condensed phase in the structural configurations shown in Fig. 1. [17, 18].

The dissolution of any substance in methanol causes the destruction of the structure developed as a result of the binding the molecules by hydrogen bonds. In the case of electrolyte dissolution, the hydrogen bond cleavage occurs between methanol molecules, and this is followed by the specific action of ions upon the molecules of the solvent. The effect of this action is the formation of certain configurations of methanol molecules around ions and electrolyte molecules known as solvation which in turn, brings about a stabilization of the solution structure.

BOCKRIS considers solvation to be a dual-natured process. Primary solvation is effected by the stabilization of certain dipole orientations of the solvent molecules around an ion and their binding with the ion as a result of the action of the ionic electrostatic field. This binding is so strong that the

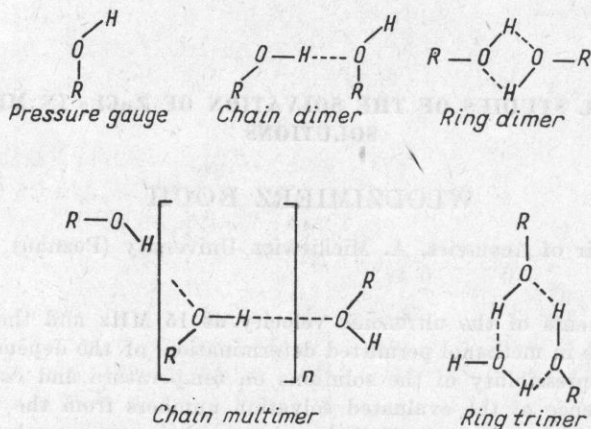


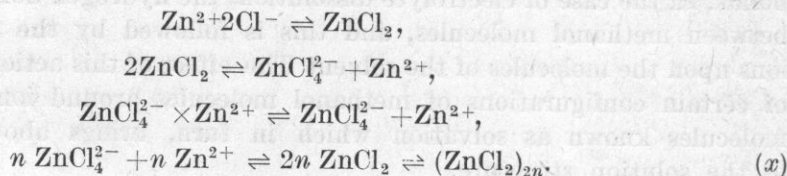
Fig. 1. Structural configurations of methyl alcohol

in its translatory motions moves along with a solvation envelope. Secondary solvation consists in the polarization of further layers of the solvent and leads to a reduction in the dielectric constant in the region surrounding the ion, thus intensifying the action of the ion upon the solvent molecules.

Solvation resulting from the electrostatic action of the ionic electric field upon the solvent leads to a reduced compressibility of the solution [10-12]. The competitive effect is the destruction of the solvent structure by ions and electrolyte molecules introduced. This effect is primarily mechanical and depends on the size of the ions [13].

As a result of increasing the electrolyte concentration, the inter-ionic distances decrease and this permits the strong attraction of ions of opposite charges. In weak electrolytes the dissociation (ionization) decreases, while in strong electrolytes ions with opposite sign (gegenions) form a dipole, a pair of ions held together by electrostatic forces. In the limiting case, the ions partly lose their solvation envelopes and come into direct contact with each other, thus forming a contact pair of ions. The likelihood of the formation of pairs of ions increases with increasing electrolyte concentration.

Zinc chloride can exist in methanol solutions in the form determined by the following equation of equilibrium:



A thorough study, chiefly using Raman spectroscopy has led to the conclusion [14-20] that in most cases zinc chloride occurs in methanol solutions in the forms determined by equilibrium (x), that is to say as ions Zn^{2+} , complex ions $ZnCl_4^{2-}$, complexes such as $ZnCl_2L_4$ or $ZnCl_2L_2$ (where L is the ligand of the solvent), and also in the form of quasi-polymer chains $(ZnCl_2)_{2n}$. The comparatively large number of forms in which zinc chloride occurs in solution is the reason for the considerable solvation effect which can be expressed as a changing of the adiabatic compressibility of the solutions.

The velocity of ultrasonic waves of infinitely small amplitude, i. e. such that the particle velocity amplitude in the wave is much less than the ultrasonic phase velocity, can be expressed via the density ρ and the adiabatic compressibility coefficient β_s in the form of Laplace formula

$$c = \sqrt{\frac{1}{\rho\beta_s}}. \quad (1)$$

The simultaneous measurement of the phase velocity of sound propagation and of the medium density permit univocal determination of the adiabatic compressibility using formula (1). At the present time this is the only method of determining, in a simple manner, the adiabatic compressibility of liquids.

The dissolution of the electrolyte changes the compressibility of the solvent mainly as a result of solvation. Proceeding from DEBYE's considerations [21], PASYNSKI [22, 23] assumes that solvation complexes can be replaced by an effective solvated *volume* which is incompressible, while the compressibility of the remaining volume of the solution is equal to that of the pure solvent. It is thus possible to determine the solvation number, i. e. the number of molecules of solvent bonded with one electrolyte molecule, from the expression

$$Z = \frac{M}{M_0} \left(1 - \frac{\beta_s}{\beta_{s0}} \right) \frac{1-g}{g}, \quad (2)$$

where M is the molecular weight of the dissolved substance, M_0 — the molecular weight of the solvent, β_s — the adiabatic compressibility of the solution, β_{s0} — adiabatic compressibility of the solvent, and g — the liquid concentration by weight.

Determination of the adiabatic compressibility by the method mentioned above thus permits calculation of the solvation numbers.

2. Method and results of the investigations

The methanol used in the experiments was dehydrated by means of magnesium with a suitable addition of iodine and then distilled twice. The efficiency of the dehydration was tested with a small iodine crystal. The zinc chloride

used was dried for 18 hours at a temperature of 120°C. Substances prepared in these ways were used to make solutions with concentrations from 0.1 to 3.0 mol/l. The maximum error in the evaluation of the solution concentration was equal to 75×10^{-4} mol/l.

The measurements of the ultrasonic phase velocity were made at 15 MHz by means of an impulse-phase interferometer type UI-13, produced by IPPT PAN in Warsaw. To avoid evaporation of the solvent and, consequently, changes in the concentration of examined liquids, the measurement vessel was additionally sealed. The results of measurements of the ultrasonic velocity had a relative error not exceeding 2×10^{-3} .

The density of the liquids examined was determined by a picnometric method with an error of no more than 5×10^{-4} .

The temperature control system comprised the Höppler thermostat connected by rubber hoses to the measurement vessel. All parts of the system were additionally insulated thermally with a felt layer 15 mm thick. The liquids used for thermostatic control were the antifreeze «Borygo» at negative temperatures, and water at positive temperatures. The negative temperatures were obtained by the immersion of the thermostat in a vessel filled with a mixture of disintegrated solidified carbon dioxide (dry ice) and «Borygo» liquid. Temperature measurements were made with a graduated thermistor type ZE-3 operating in a Wheatstone bridge system. The temperature control system used permits evaluation of the temperature of an examined solution to an accuracy of 0.1°C. The temperature range of the measurements was from -20°C to 60°C.

The results of the measurements of ultrasonic velocity in solutions of zinc chloride in methanol are shown in Fig. 2.

From these measurements and those of solution density, the values of the adiabatic compressibility of the tested solutions were calculated. The results of these calculations are graphically represented in Figs. 3 and 4.

The dependence of the adiabatic compressibility on the temperature and the solution density has been thoroughly analyzed to find the analytical form of the functions $\beta_s = \beta_s(t)$ and $\beta_s = \beta_s(k)$. It was found that both functions are of exponential character. From the numerical calculations made for all concentrations it results that the functional formula $\beta_s = \beta_s(t)$ for a given solution concentration can take the form

$$\beta_s(t) = \beta_s \exp \mu(t-t_0), \quad k = \text{const}, \quad (3)$$

where $\beta_s(t)$ is the adiabatic compressibility at temperature t , β_s is the adiabatic compressibility of the solution at the lowest temperature of measurement $t_0 = -20^\circ\text{C}$, and μ is the temperature coefficient of the adiabatic compressibility of the solution.

Taking logarithms of the previous equation, we obtain

$$\log \beta_s(t) = \log \beta_s + \mu(t-t_0) \log e = \text{const} + (\mu \log e)t. \quad (4)$$

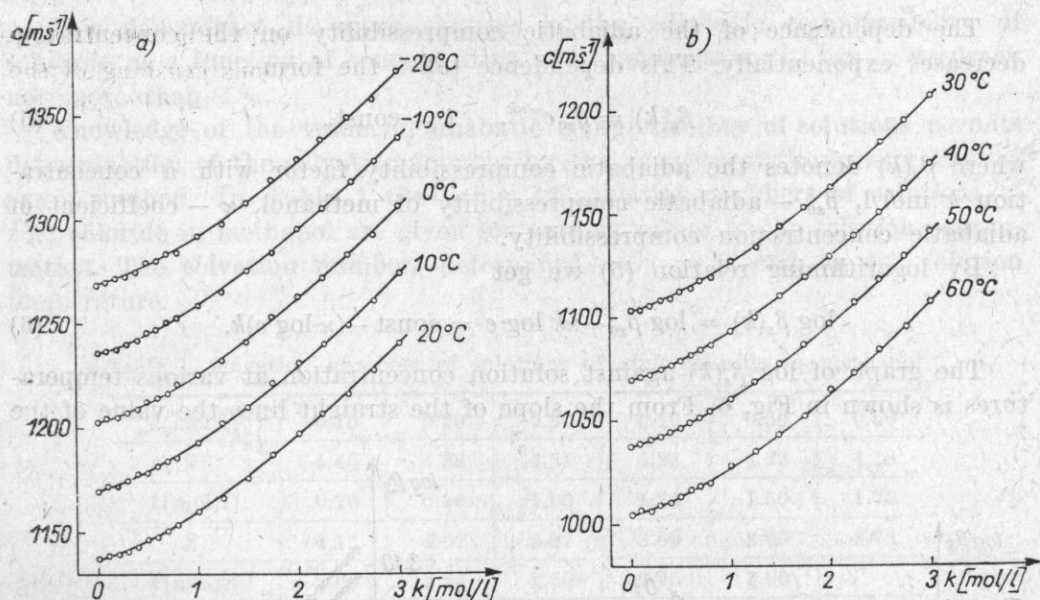


Fig. 2. Variation of ultrasound velocity with zinc chloride concentration for solutions in methanol

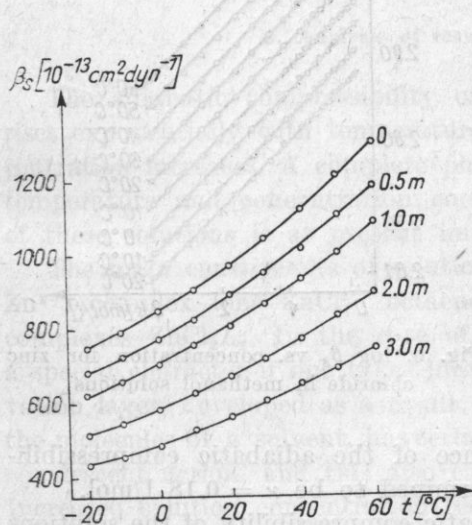


Fig. 3. Adiabatic compressibility vs. temperature for zinc chloride in methanol solutions with different concentrations

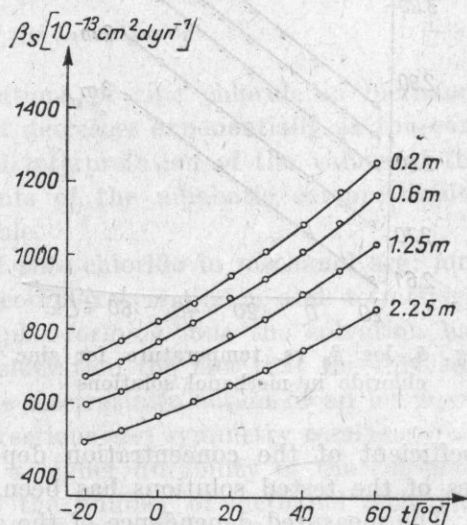


Fig. 4. Adiabatic compressibility vs. temperature for zinc chloride in methanol solutions with different concentrations

The value of the coefficient μ can be determined from the slope of the straight lines on the graph of $\log \beta_s(t)$ against temperature (t). This dependence is shown in Fig. 5 for various solution concentrations. The value obtained from the graph for the temperature coefficient of the adiabatic compressibility of zinc chloride solutions in methanol has a value of $\mu = 68 \times 10^{-4} \text{deg}^{-1}$.

The dependence of the adiabatic compressibility on the concentration decreases exponentially. This dependence takes the form

$$\beta_s(k) = \beta_{s0} e^{-\kappa k}, \quad t = \text{const}, \quad (5)$$

where $\beta_s(k)$ denotes the adiabatic compressibility factor with a concentration k mol/l, β_{s0} — adiabatic compressibility of methanol, κ — coefficient of adiabatic concentration compressibility.

By logarithming relation (5) we get

$$\log \beta_s(k) = \log \beta_{s0} - \kappa k \log e = \text{const} - (\kappa \log e)k. \quad (6)$$

The graph of $\log \beta_s(k)$ against solution concentration at various temperatures is shown in Fig. 6. From the slope of the straight lines the value of the

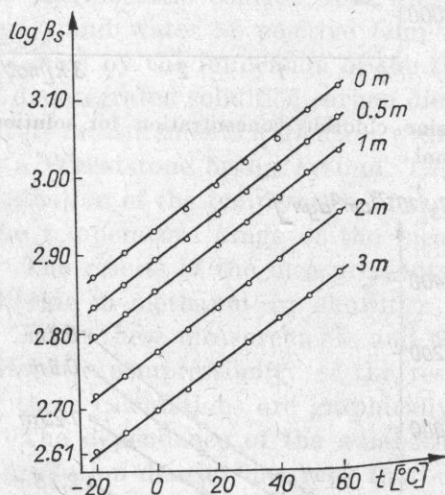


Fig. 5. $\log \beta_s$ vs. temperature for zinc chloride in methanol solutions

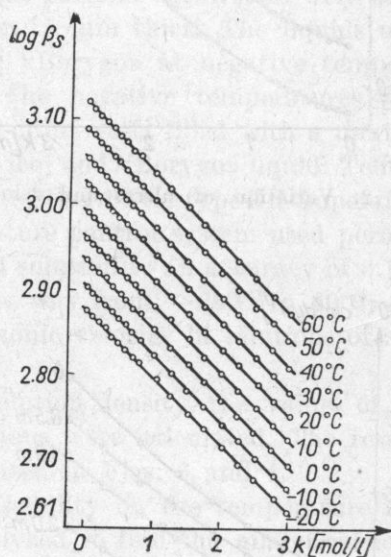


Fig. 6. $\log \beta_s$ vs. concentration for zinc chloride in methanol solutions

coefficient of the concentration dependence of the adiabatic compressibilities of the tested solutions has been determined to be $\kappa = 0.18$ l/mol.

The measured dependence of the adiabatic compressibility of the solutions on the temperature and concentration can take one functional form for the range of concentrations and temperatures used in the investigations,

$$\beta_s(t, k) = \beta_{s0} \exp [\mu(t-t_0) - \kappa k], \quad (7)$$

where β_{s0} is the adiabatic compressibility of methanol at a temperature $t_0 = -20^\circ\text{C}$, and $\beta_s(t, k)$ — the adiabatic compressibility of a solution of concentration k mol/l at a temperature of $t^\circ\text{C}$.

This dependence describes changes in the adiabatic compressibility of solutions as a function of concentration and temperature with an inaccuracy not more than 1%.

Knowledge of the value of adiabatic compressibility of solutions permits determination of the solvation number by the acoustic method using PASYNSKY'S method. In Table 1 the values of solvation numbers of solutions of zinc chloride in methanol are given for various values of the solution concentration. The solvation numbers determined do not depend on the solution temperature.

Table 1. Solvation numbers of solutions of zinc chloride in methanol

$k[\text{mol/l}]$	0.10	0.20	0.30	0.40	0.50	0.60
Z	4.45	4.38	4.31	4.28	4.23	4.18
$k[\text{mol/l}]$	0.70	0.80	1.00	1.25	1.50	1.75
Z	4.13	4.07	3.97	3.89	3.80	3.73
$k[\text{mol/l}]$	2.00	2.25	2.50	2.75	3.00	
Z	3.64	3.50	3.39	3.29	3.20	

3. Analysis of results of the investigation

The adiabatic compressibility of solutions of zinc chloride in methanol rises exponentially with temperature and decreases exponentially as the concentration increases. A complete physical interpretation of the values of the temperature and concentration coefficients of the adiabatic compressibility of these solutions is at present impossible.

The main constituents of solutions of zinc chloride in methanol are: ions Zn^{2+} , complex ions ZnCl_4^{2-} octaendric complexes ZnCl_2L_4 , and tetraendric complexes ZnCl_2L_2 . In the case of complex-forming ions the solvation has a special character if one takes into consideration the fact that the first solvation layer, developed as a result of the electrostatic action of an ion upon the molecules of a solvent, has certain directions and symmetry resulting from covalent action, and this also causes a higher durability of the complex. Increased solution concentration reduces the number of methanol molecules per ZnCl_2 -molecule. Thus in a solution of concentration 0.1 mol/l there are 247 methanol molecules per ZnCl_2 -molecule, while in a solution with concentration 3.0 mol/l there are only 8 methanol molecules. Such a considerable change in the ratio of the numbers of molecules does not, however, effect an equally considerable change on the solvation numbers.

The solvation number varies from 4.45 for a concentration of 0.1 mol/l to 3.20 for a concentration of 3.0 mol/l, having an average value of 4. Such an insignificant change of the solvation number is an explicit proof of the

establishment in the solution of very durable solvation complexes. The negligible decrease of the solvation number with increasing solution concentration results only from the «competitive» action of the ions in methanol molecule binding in the solvation envelope, since the relative number of these molecules decreases considerably with increasing solution concentration. The independence of the solvation number from the temperature also evidences the considerable durability of the developing solvation complexes. The intensification of the thermal motion of the methanol molecules (the ions) with increasing temperature does not cause any change in the solvation numbers.

It seems that the complex ions $ZnCl_4^{2-}$ predominate in the solvation process. This conception is supported by the independence of the solvation numbers from the temperature (complex ions development very stable solvation complex) and by the fact that the value of the solvation number is about 4. This would suggest that a complex ion binds four methanol molecules in quasi-hydrogen bonds. The share of other forms of zinc chloride, encountered in the solution in the solvation process, seems to be negligible. The ions Zn^{2+} , on one hand, act electrostatically upon the methanol molecules, while, on the other hand, being large ions, destroy the mechanical structure of the methanol. Both effects are competitive effects and seem to bring about a total insignificant effect in the solvation process.

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