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Ultrasound velocity measurements in liquid media

B. Voleišienė, A. Voleišis

Kaunas University of Technology, Prof. K. Baršauskas Ultrasound Research Institute,

(E-mail: birute.voleisiene@.ktu.lt)

Abstract:

This review is a survey of the authors` scientific investigations in the field of ultrasound velocity measurements in electrolyte solutions and various liquid systems. Measurements were performed with a specially designed ultrasonic-laser interferometer and a pulse-echo system. The main molecular acoustic interferometric experiments were provided in aqueous solutions of nine lanthanide nitrates and six sulphates within the frequency range of 3÷200 MHz. The rear earth elements from lanthanum (57) to lutecium (71) are the ideal group for investigation of the ion-ion interaction as well as influence of ion field on the solvent structure. Data of ultrasound velocity dispersion at different temperatures and concentrations are interpreted as being due to the process of association of lanthanide (III) ions and ligands and formation of inner sphere complexes $[LnNO_3]_{aq}^{2+}$ and $[LnSO_4]_{aq}^{+}$. Kinetic parameters for the formation of inner sphere complexes have been determined. Non monotonic variation of the hydration number was obtained for lanthanide nitrate solutions across the series. Measurements in the synovial and cerebrospinal fluids were provided with the aim of disease diagnostics, in blood – for coagulation studies. Water-glycol mixtures were proposed as reference media, acrylamide polymerization - as a phantom for blood clotting. Some investigations were provided for the application in the control of technological processes.

Keywords: ultrasonic interferometer, pulse-echo, dispersion, chemical relaxation, medical-biological, polymerization, reference media.

Introduction

Ultrasonic waves, i. e. associated pressure and adiabatic temperature oscillations, disturb the equilibrium between solvent and solute molecules. These retarded equilibrium shifts between different molecular configurations or hydrated ions substitutions affect, in turn, the ultrasound velocity and absorption. Relaxation behaviour can be observed as well. In this way ultrasonic spectrometry permits the study of complexation processes in solution and the extraction of specific relaxation parameters of a chemical equilibrium. These studies have been summarized in various review articles and books [1-4]. Application of acoustic methods have showed extensive possibility in the fields of solution chemistry, physical chemistry, biochemistry, chemical engineering and process control for a fundamental understanding of many phenomena in solutions and liquid systems [5-6].

It is also possible to estimate the hydration numbers of the electrolyte solutions from the molar compressibility value at infinite dilution. Metal ions play an important role in chemical and biological systems so the hydration of ions in these systems is a key issue to understand the chemical and dynamical processes [7-8]. Beside widespread well established studies of the compressibility behaviour of liquids in basic research, more recently the adiabatic compressibility has also been considered as an indicator with high potential in the advanced medical diagnoses and as a process control parameter in the food industry [9]. For the last decade, solvation processes of metal ions have been extensively studied using various techniques [10-16]. Despite a large amount of works, there are no strict structural models of electrolyte solutions, nor well-substantiated parameters of ion hydration spheres [17]. Dissolution of an electrolyte in water is accompanied by electrostriction of the solvent under the action of the electrostatic fiels of newly formed ions. Change in the compressibility of the solution serves as a measure of ions hydration in ultrasound methods [18-20].

In this paper first of the all we present detailed summary of interferometric ultrasound velocity dispersion measurements in lanthanide electrolyte solutions over a wide frequency range and the analysis of the experimental data – determination of rate constants of fast chemical reactions, investigation of hydration phenomenon in these solutions in order to explain a specific dependence of relaxation parameters across the series. As was emphasized by other authors [5, 6, 9, 21], our approach was unique and became possible due to the high accuracy of measurements.

Another group of experiments concerns ultrasound velocity measurements in biological liquids: synovial and cerebrospinal fluids with the aim of disease diagnostics, for blood coagulation studies, as well as acrylamide polymerization, etc. The latter pulse-echo measurements were provided in single and multi-channel small volume (<1 ml) chambers. The multi channel approach revealed more detailed and unexpected information about the clot formation and the chemical polymerization processes, which are very similar from the ultrasonic point of view.

Some experiments concern investigations of water-glycols mixture reference media and for the application in the control of technological processes.

Measurement methods

Two methods were used for the ultrasound velocity measurements in liquid media: interferometric and pulse-echo. The interferometric method is traditional and more suitable for precise absolute measurements over a frequency range, while the pulse-echo is convenient for the determination of ultrasound velocity variations in small volumes.

Interferometric method

Especially for these investigations ultrasonic laser interferometer was developed. The block diagram of the interferometer is represented in Fig. 1. Our objective was to achieve a high accuracy of the measurements over a wide frequency range with the same acoustic system. It is essential from the point of view of possible medium contamination as well as temperature stability during the experiment.

In a double crystal ultrasonic interferometer the change of the distance between the transmitter 3 and the receiver 5 is measured by a single beam laser feed-back interferometer. It consists of laser 8 and external moving mirror, which in our case is piezoreciever 5.

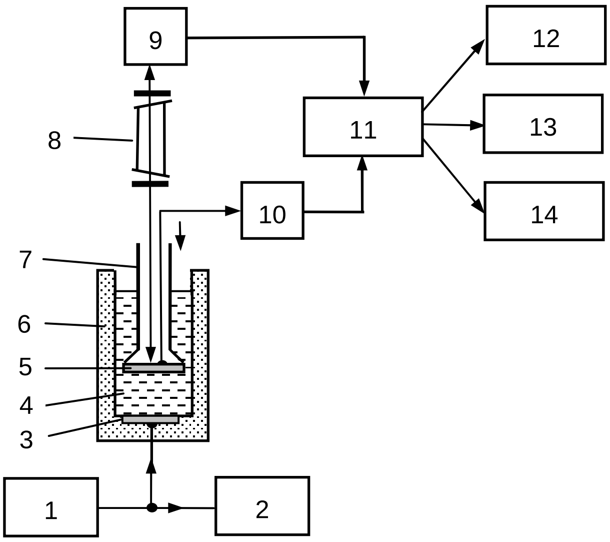


Fig. 1. **Block diagram of the ultrasonic laser interferometer: 1 – high frequency generator, 2 – frequency meter, 3 – sending quartz crystal, 4 – liquid medium, 5 – receiving quartz crystal, 6 – water bath, 7 – moving part, 8 – He Ne laser, 9 – photodetector, 10 – amplifier and acoustic signal detector, 11 – computing unit, 12 – acoustic half-wave indicator, 13 – ultrasound velocity indicator, 14 – entire record**

During the measurement process the moving part 7 with the receiving quartz crystal 5 descends smoothly by means of a hydraulic arrangement thus escaping vibrations. At the output of the photodetector 9 a harmonic signal with the period Λ/2 is observed, where Λ=0.6328198 μm is the laser wavelength in "normal" air. In the computing unit 11 displacement marks up to Λ/8~0.08 μm or even Λ/16~0.04 μm are formed. The Marks value is selected depending on acoustic half-wave signal peaks quality (sharpness) and the S/N ratio. So, the standing ultrasound half-wave is continuously measured with the quantization usually equal 0.079102 μm and is indicated in the block 12. At a given frequency f (MHz) and certain ultrasound half-wave number N ultrasound velocity the digital value is proportional to the corresponding change of the acoustic path, expressed as a number of laser interferometer displacement marks. The number N in the case of interpolation up to Λ/8 can be found from the expression:

$$N=(\Lambda\times f)/(4\times\Delta c), \tag{1}$$

where Δc is the ultrasound velocity measurement quantization (m/s). If Δc=0.01 m/s the relation (1) can be expressed as follows:

$$N=15.82049\times f, \tag{2a}$$

$$f=0.0632092\times N. \tag{2b}$$

It means, that digital ultrasound velocity measurements can be provided simply every 63.209 kHz. For example, in the region of 10 MHz such combinations of f and N are possible (Table 1):

Table 1. **Possible combinations of frequency *f* and halh-wave number N in the region of 10 MHz**

	f	N
1	9.92384	157
2	9.38705	158
3	10.05026	159
4	10.11347	160
5	10.17668	161

Before the measurements the best frequency from the acoustic point of view must be selected and adjusted according to Eq. 2a and b. The necessary number N is introduced manually into the computing unit 11.

The acoustic path in the interferometer can be changed in the interval 6 cm→0. For a single measurement of the ultrasound velocity (1500 m/s) with the quantization of 1 cm/s the necessary displacement is equal 11.86 mm. So, the velocity can be determined from various intervals of standing waves peaks. The measurement cycle is initiated automatically at any predetermined distance between the crystals and lasts ~20 seconds. For ideal measurement conditions (absence of diffraction, high temperature stability, etc.) the results must be identical within the experimental error. The interferometer enables measurement of the position of each possible standing wave peak of the ultrasonic interferometer by means of laser marks. Data are registered in the block 11 for further processing in order to determine ultrasound velocity values from various peak intervals for their comparison. Some experiments were reported in [22]. At the frequency 17.0665 MHz (N=270) more than 180 velocity results in water were obtained during 6 cm displacement of a piezoreceiver. All results are situated around 1484.08 m/s within the window ±0.03 m/s.

Comprehensive investigations of metrological characteristics of the interferometer allow argue that the measurement error at medium ultrasonic frequencies is of order 0.001-0.002 %. At low frequencies (<15 MHz) experimentally determined diffraction corrections were introduced. They were significantly lower when crystals operated with a lower sensitivity far from the resonance. At frequencies above 100 MHz the velocity quantization value may fall to 0.2 m/s in concentrated electrolyte solutions in the relaxation region. So, for a better accuracy results of repeated measurements (sometimes to 30) were averaged.

The acoustic system consists of highly identical polished X-cut quartz crystals, operating on odd harmonics and thus overlaping a wide frequency range. Identity of the crystals means the same diameter and thickness, and especially resonance and antirezonance frequencies (up to 0.001 %). Pairs of 1 MHz, 2.8 MHz, 4 MHz and 10 MHz quartz crystals were used, depending on the required density of experimental points in the given frequency range. Thus, if the low-frequency relaxation was investigated, 1 MHz crystals were used. An optimal precision of measurements over a frequency range provides a pair of composite crystals, consisting of Ø 40mm 1 MHz ring with Ø 10 mm 10 MHz crystal precisely mounted in the center. At low frequencies operate 1 MHz crystals, at high (e.g.>70 MHz) – 10 MHz crystals. Ultrasound velocity dispersion in electrolyte solutions is notoriously small so the investigations require a high measurement accuracy. Over 200 MHz measurements with the necessary accuracy are problematic due to a high absorption and small possible acoustic path (1 mm and less). Meanwhile acoustic experiments in distilled water were provided up to 1250 MHz. With a pair of 2.8 MHz quartz crystals a perfect standing wave picture was recorded at 1004 MHz (359-th harmonic) in the interval between crystals 135 μm →0. At 404 MHz (145-th harmonic) experiments showed, that all distances between adjacent peaks in the displacement interval 1 μm →0 are stable within the measurement quantization ±Λ/8. It means the best possible velocity measurement quantization ±0.15 m/s in the liquids of low absorption (as water) [23].

The temperature was kept with an accuracy of ±0.005^o C and was measured with calibrated Hg thermometers with the resolution of 0.01^{o}C. All necessary corrections (immersion depth, inclination, air pressure, etc.) were introduced.

The solutions were prepared by weighting bidistiled water and commercial salts without further purification. The concentration of the cation was determined by EDTA titration using Xylenol Orange as the end-point indicator. Each analysis, made in triplicate, gave a mean deviation less than 1%.

The interferometer and the experimental procedures have been described elsewhere [24-28]. A micro computer-based version of the interferometer was developed as well [29, 30]. Practically data processing is performed in a real time. Acoustic $\lambda/2$ measurement results are represented on the screen in the forms of graph and histogram with its parameters: maximum, minimum and mean values, standard and mean errors S and σ. In the same form (graph+histogram) are represented ultrasound velocity results, obtained from the entire record data (14 block) by shifting $N\times\lambda/2$ interval. Graphical representation of information enables one to detect systematic errors, explain their sources and eliminate them. The graph of velocity values is a very sensitive indicator of the quality and optimal parallelism adjustment of the acoustic system. Minute misadjustment leads to systematic errors and can be revealed. This method of processing the measurement information enables to ground metrologically the obtained ultrasound velocity value.

On the basis of this interferometer a computerized version for ultrasound absorption measurements in liquids was investigated as well [31, 32]. The peculiarity of the system is the measurement of the width of each resonance peak at the level 0.707 and corresponding half-waves by the He-Ne laser. The obtained data are represented on the screen in the form of graphs αl and $\alpha\lambda$ as functions of wave numbers and corresponding histograms with their parameters. Here α is the absorption coefficient of the medium tested, l is the distance between quartz crystals, wavelength λ is determined during this experiments. The first experiments were provided in low absorption liquid (distilled water) at 14.12 MHz and demonstrated good results. Measurements of ultrasound absorption and velocity are provided simultaneously.

Pulse-echo method

The interferometric method is precise and especially suitable for determination of absolute values of ultrasound velocity. In the case, when the changes of structure of the liquid medium are investigated, e.g. blood coagulation, chemical polymerization, etc. any movable parts can`t be inside the measurement chamber. More, the chamber volume often must be less than 1 ml. So, the interferometer of variable path can`t be used. For these experiments the differential pulse-echo method for measurements in small volumes of medium was developed [33÷40]. In the first realization ultrasonic pulses were transmitted into the investigated sample through a buffer rod. Two reflections are observed: from the interface buffer rod/liquid medium and from the bottom of the measurement chamber. The delay time $\Delta\tau$ in an ultrasonic transducer and electronics is eliminated in this differential approach. The ultrasound velocity in the medium is found from the measured delay time difference and earlier found length of the measurement chamber. The length is found by a calibration procedure. It means the measurements in distilled degassed water precisely at the same temperature and calculations using standard ultrasound velocity value tables [41]. In a multi-channel approach [38, 40], which is essential for obtaining more information about the changes of the medium structure, delay rods are inconvenient to use. Differential measurements are realized easily using the first and the second reflections from the chamber wall and the transducers directly contacting with the medium. The acoustic path length is determined for each channel.

The last version of the multichannel 0.7 ml volume chamber with a four element linear array is shown in Fig.2.

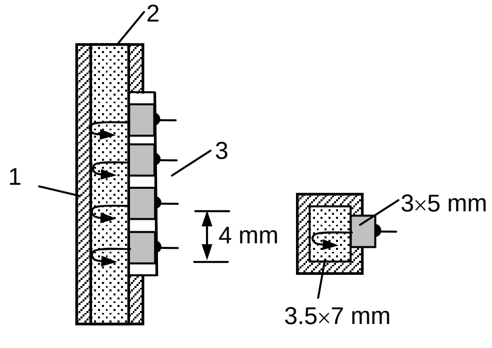


Fig. 2. **Four channel 0.7 ml volume chamber with 5 MHz linear array: 1 – signal reflecting wall, 2 – liquid medium, 3 – array**

It is designed for the investigation of gravitation influence on the blood coagulation and acrylamide polymerization reaction course. For biocompatibility its inner surfaces are gold coated. The array elements are 3×5 mm, the distance between adjacent elements is 1 mm. Acoustic $\lambda/4$ maching layer and light damping are used. The pulse response consists of ~1.5 period of signal and is wideband. The resolution of ultrasound velocity measurements is ±3 cm/s, experimentally observed random variations of the ultrasound velocity in distilled water were ±5 cm/s.

Photo of the measurement chamber is shown in Fig. 3.

Fig. 3. **Photo of the four-channel 0.7 ml volume chamber, immersed in a water bath during the experiment**

Molecular acoustics investigations

Ultrasonic velocity dispersion study in aqueous solutions of lanthanide and yttrium salts

The aim of experiments in molecular acoustics is to find the correlation between acoustic parameters of solutions (ultrasound velocity, its dependence on frequency) and their structure. For this purpose lanthanide salts were chosen. Lanthanide, i.e. the elements of atomic number Z from 57 (lanthanum) to 71 (lutecium) form the unique series within the Periodic Table. Together with scandium and yttrium these metals display a predominantly trivalent chemistry. In the rare earth elements series ionic radius decreases monotonically due to lanthanide compression, therefore rare earth elements are the ideal group for investigation the ion-ion interaction as well as influence of ion field on the solvent structure. In recent years rare earth elements and their salts become more used in various areas. For example: lanthanide (III) ions are often used as structural probes in biological systems to obtain some information on the binding sites of “vitality” elements such as Ca, Mg, Mn, Mo, V and others that are formed in coordinated complexes of humane organism; terbium (III) and europium (III) are used as luminescent probes, while gadolinium (III) is an effective proton relaxation agent [42-44]. Also, their use in technology is growing rapidly as their properties are more fully explored [45].

Lanthanide nitrates, sulphates, chlorides, bromides and yttrium nitrate solutions have been studied [25-28, 46-50]. The ultrasound velocity dispersion was investigated in aqueous nitrate solutions of trivalent ions of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Er^{3+}, Y^{3+} (in the frequency range of 3÷200 MHz) and in sulphates of La^{3+}, Ce^{3+}, Nd^{3+}, Gd^{3+}, Er^{3+} and Yb^{3+} (3÷100 MHz). A single relaxation was observed for the systems involved. As an illustration, Fig. 4 shows the theoretical dispersion curve which fitts the experimental points for $Y(NO_3)_3$ at the concentration 0.2 mol/l. Here the ultrasound velocity at low frequencies is c_0 =1498.88 m/s, at high frequency c_∞ =1500.40 m/s and the relaxation frequency f_R = 69 MHz (corresponds to the inflection point of the curve).

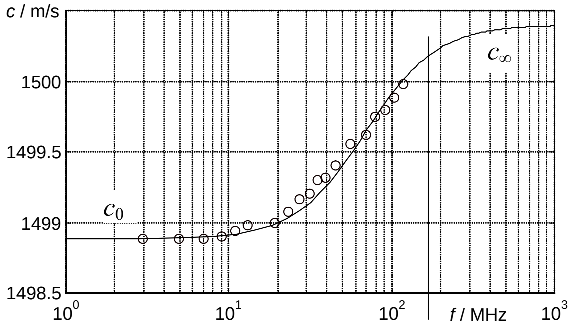


Fig.4. **Dispersion curve for $Y(NO_3)_3$ at concentration 0.2 mol/l at 20ºC**.

Experimental results for the tested nitrates of various concentrations at 20^0 C are listed in Table 2, for sulphates – in Table 3, where f_R is the relaxation frequency, $(c_\infty - c_0)$ is the dispersion value, $(c_\infty - c_0)/(c_0 \times C)$ is the total molar dispersion.

Table 2. **Relaxation parameters of nine lanthanide and yttrium nitrate solutions at 20º C.**

Electrolyte	C, mole/l	f_R, MHz	c_∞-c_0, m/s	$(c_\infty-c_0)/(c_0 \times C)$, 10^{-4} l/mol
$La(NO_3)_3$	0.048	36	0.32	44.9
	0.092	37.5	0.90	65.7
	0.176	40	2.75	105
$Ce(NO_3)_3$	0.043	41	0.54	82.5
	0.088	43	1.50	115
	0.180	44.5	3.50	130
$Pr(NO_3)_3$	0.050	45.5	0.82	110
	0.100	47	2.30	155
	0.194	50	5.03	177
$Nd(NO_3)_3$	0.050	47	0.87	117
	0.099	49	2.15	146
	0.194	52	4.70	163
$Eu(NO_3)_3$	0.052	45	1.10	143
	0.105	48	2.30	147
	0.200	52	2.75	92.5
$Sm(NO_3)_3$	0.195	56	3.70	128
$Gd(NO_3)_3$	0.047	32.5	0.35	50.2
	0.089	32.5	0.54	41.8
	0.171	32.5	1.42	56.0
$Dy(NO_3)_3$	0.109	30	0.26	16.1
	0.194	30	0.54	18.8
	0.495	30	2.55	34.5
$Er(NO_3)_3$	0.192	20	0.46	16.1
	0.318	20	1.12	23.9
	0.464	20	2.24	32.5
$Y(NO_3)_3$	0.10	63	0.66	44.2
	0.20	69	1.52	50.7
	0.30	72	3.90	86.2

Ultrasonic velocity dispersion it is considered to be due to the process of association of lanthanide ions with NO_3^{-1} or SO_4^{-2} and formation of inner-sphere complexes $LnNO_3^{+2}$ or $LnSO_4^{+}$. We accept the modified two-step mechanism proposed by Eigen and Tamm for the studies of the complexation of many metal ions in water or mixed solvents [1]:

$$M_{aq}^{m+} + L_{aq}^{n-} \overset{\text{step I}}{\underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}}} M^{m+}(H_2O)_xL^{n-} \overset{\text{step II}}{\underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}}}$$

$$(ML)_{aq}^{m-n} + H_2O\,. \qquad (3)$$

Table 3. **Relaxation parameters of six lanthanide sulphate solutions**

Electrolyte	*C*, mole/l	f_R, MHz	c_∞-c_0, m/s	$(c_\infty$-$c_0)/\ c_0\times C$, 10^{-4} l/mol
$La_2(SO_4)_3$	0.0035	13.5	0.38	732.4
	0.065	13.5	0.76	788.6
	0.012	13.5	1.84	1034
$Ce_2(SO_4)_3$	0.005	12.2	0.74	998.3
	0.010	15.8	1.30	876.8
	0.020	20.0	2.60	876.6
$Nd_2(SO_4)_3$	0.0055	17.5	0.71	870.9
	0.0099	19.0	1.40	954.1
	0.0201	22.0	3.16	1065
$Gd_2(SO_4)_3$	0.004	23.0	0.58	978.4
	0.0085	27.0	1.08	857.4
	0.016	32.0	2.48	1046
$Er_2(SO_4)_3$	0.0052	5.5	0.60	778.4
	0.001	5.8	1.00	674.7
	0.020	6.0	2.08	701.0
$Yb_2(SO_4)_3$	0.0095	2.7	1.03	731.5
	0.0199	2.9	1.98	983.2
	0.039	3.2	3.58	619.5

The step I represents diffusion - controlled association of the two ions to form a solvent separated outer sphere complex coupled to solvent loss from the inner solvation shell of the ligand. The step II represents solvent loss from the cation solvation shell and formation of inner sphere $[ML]^{m-n}$ complex. Here k_{12}, k_{23} are forward rate constants and k_{21}, k_{32} are reverse rate constants for a reaction Eq.1. We have attributed the observed relaxation frequency to the second step. Relaxation frequency cannot be confined to the step I as theoretically estimated rate constants for a diffusion controlled association would give about 10^9 – 10^{10} l/mol·s. Such value predicts relaxation frequency of an order of magnitude higher than that observed in this work.

The experimental results show that for solutions of $La(NO_3)_3$, $Ce(NO_3)_3$, $Pr(NO_3)_3$, $Nd(NO_3)_3$, $Eu(NO_3)_3$, $Y(NO_3)_3$ and for $Ce_2(SO_4)_3$, $Nd_2(SO_4)_3$, $Gd_2(SO_4)_3$, $Yb_2(SO_4)_3$ relaxation frequency slightly depends on concentration. The rate constants k_{23} and k_{32} were calculated according to Eigen`s theory [1]. The rate constant k_{23} is interpreted as the rate exchange of a water molecule in the first coordination sphere of the cation with ligand in the second coordination sphere; k_{32} is the rate for reverse process, so k_{32} will be dependent on the nature of the anion. Table 4 lists the rate constants k_{23} and k_{32} obtained from the studies of investigated electrolyte solutions.

The rate constants k_{23} measured in our work by ultrasonic method closely correspond to the rates for the exchange of labeled water molecules from the inner coordination spheres of the lanthanide(III) ions, determined by ^{17}O-NMR relaxation and chemical shift measurements [51-52].

Table 4. **Values of k_{23} and k_{32} rate constants**

Electrolyte	$k_{23}\times10^{-8}$, s^{-1}	$k_{32}\times10^{-8}$, s^{-1}
$La(NO_3)_3$	8.8	1.76
$Ce(NO_3)_3$	10.0	1.92
$Pr(NO_3)_3$	11.2	2.14
$Nd(NO_3)_3$	12.0	2.20
$Eu(NO_3)_3$	11.6	2.15
$Y(NO_3)_3$	1.2	2.75
$Ce_2(SO_4)_3$	0.57	0.15
$Nd_2(SO_4)_3$	1.27	0.45
$Gd_2(SO_4)_3$	4.36	0.37
$Yb_2(SO_4)_3$	0.21	0.06

Assuming the dispersion in lanthanide nitrate and sulphate solutions is caused by an association process, the magnitude of ultrasound dispersion may be the quantity of complexation. It is evident from Fig. 5 where ultrasound velocity dependence on concentration in $Ce_2(SO_4)_3$ and $Ce(NO_3)_3$ solutons is shown [53]. For $Ce_2(SO_4)_3$ they are distinguished into three curves: $c_0 = \varphi(C)$, $c_\infty = \varphi(C)$ and $c_R = \varphi(C)$,where c_R is the ultrasound velocity at the relaxation frequency. From data of the curves it is possible to determine the values of dispersion parameters (c_∞-c_0), c_R at any concentration. As seen, the magnitude of ultrasound dispersion for $Ce(NO_3)_3$ is much smaller (shaded area) than that of $Ce_2(SO_4)_3$ solutions. The lanthanide nitrates are known to form predominantly outer sphere complexes with some inner sphere substitution occurring only at high concentrations [52]. The lanthanide sulphates on the other hand form predominantly inner sphere complexes.

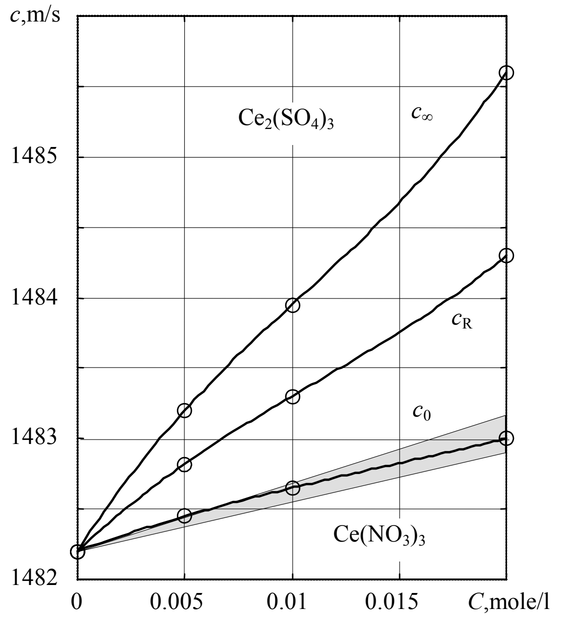


Fig. 5. **Ultrasound velocity dependencies on concentration in solutions of $Ce_2(SO_4)_3$ (c_∞, c_R, c_0) and $Ce(NO_3)_3$ (the shaded area) at 20°C**

The magnitude of the dispersion in the $Ce_2(SO_4)_3$ solutions increases with concentration of the cation and with the amount of inner complexes. In order to produce an appreciable concentration of inner complexes in the $Ce(NO_3)_3$ solutions for a similar dispersion and relaxation a tenfold higher concentrations of the nitrates must be used.

The existence of both outer and inner sphere complexes in polyvalent salts has been determined by different techniques. For example, Choppin using NMR method [54] has summarized the data on lanthanide nitrates, concluding that 27% $[LaNO_3^{2+}]_n$ inner sphere complexes exist in $La(NO_3)_3$ water solution. No dispersion we found for solutions of $LaCl_3$, $EuCl_3$, $GdCl_3$, $ErCl_3$ and $LaBr_3$ in the investigated frequency range [49, 55-57]. The absence of relaxation for these solutions suggests that in these systems lanthanide ions and Cl^{-1} or Br^{-1} are separated by solvent molecules. Moreover, the Br^{-1} is a weakly complexing anion, allow us to made the conclusion than compound La - Br does not form any inner sphere complexes in dilution aqueous solutions.

For solutions of $Gd(NO_3)_3$, $Dy(NO_3)_3$, $Er(NO_3)_3$ and $La_2(SO_4)_3$ no concentration dependence of relaxation frequency was observed. For a bimolecular second order reaction the correlation between the relaxation time τ and the forward ant reverse rate constants is expressed as follows:

$$\tau^{-1} = 2\pi fR= k23\Phi_C+ k32. \qquad (4)$$

The function Φ_C depends on the equilibrium activities of the free ions. Φ_C can be assumed constant for closely related cations such as the lanthanides. Thus τ^{-1} will depend mainly on k_{23} and k_{32} will be dependent on the nature of the anion. The sum of the constants k_{23} and k_{32} are presented in Table 5.

Table 5. **Rate constants of exchange of water molecules for some ions**

Ion	f_R, MHz	$(k_{23}+ k_{32}) \times 10^{-8}$, s^{-1}
Gd^{3+}	32.5	2.04
Dy^{3+}	30.0	1.88
Er^{3+}	20.0	1.25
La^{3+}	13.5	0.85

It is interesting to consider the parameters which influence the relaxation frequency and then atempt to interpret this dependence against cation atomic number. Fig.6 describes the dependences of relaxation frequency f_R for the investigated nitrate solutions at the concentration 0.2 mol/l across the series.

As seen, the relaxation frequency reaches a maximum on samarium and then falls down to the heaviest lanthanides. Fig.7 shows the dependence of the relaxation frequency for lanthanide sulphate solutions at concentration 0.01 mol/l against of atomic number. In this case the relaxation frequency reaches a maximum on gadolinium. Dependence of the relaxation frequency against cation atomic number cannot be explained simply in terms of changes in a cation size. The high electric field strength at the surface of the cation must greatly influence the solvent molecules or the solvent structure in the immediate vicinity of the ion. In the absence of a complete understanding of the structure and how it is influenced by the presence of ions, it is convenient to regard such structural changes as changes in the average cation coordination number. The variation of f_R is consistent with this assumption that for cations toward the center of the series, where two (or more) coordination numbers become equally probable, the change from one coordination number to another occurs more readily.

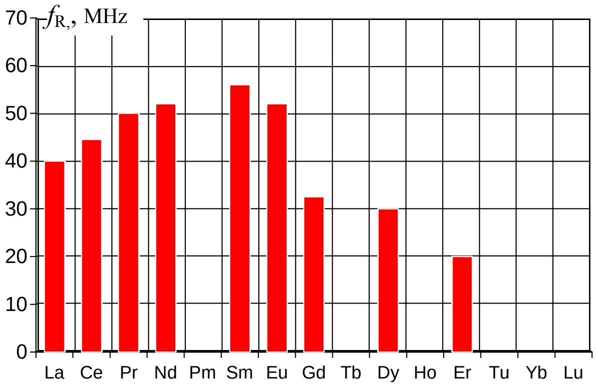


Fig. 6. **Dependence of the relaxation frequency f_R for lanthanide nitrate solutions at the concentration 0.2 mol/l across the series**

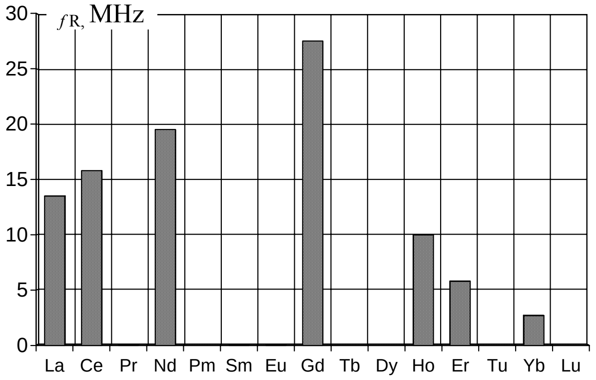


Fig. 7. **Dependence of the relaxation frequency f_R for lanthanide sulphate solutions at the concentration 0.01 mol/l across the series**

Our studies on the hydration of lanthanide nitrates in aqueous solutions indicate a change of the hydration number across the series [57].

Hydration phenomenon in lanthanide salts solutions

The variation of the hydration number Z_0 for lanthanide nitrate solutions across the series is shown in Fig. 8. The progressive filling of the 4*f* orbitals from La^{3+} to Lu^{3+} is accompanied by a smooth decrease in the ionic radius with increase in the atomic number as a consequence of the increasingly strong nuclear attraction for the electrons in the diffuse *f* orbitals. These orbitals are shielded by the surrounding filled 5s and 5*p* orbitals, leading to a very small crystal field splitting in the lanthanide complexes. Thus, the coordination properties of the Ln^{3+} ions mainly depend upon the steric and an electrostatic nature of the ligands. Hence, for solvents without covalent bonding like water, ion-solvent forces can be well represented by simple Coulomb and van der Waals terms. Radii of the lanthanide ions decrease from La to Lu (lanthanide contraction).

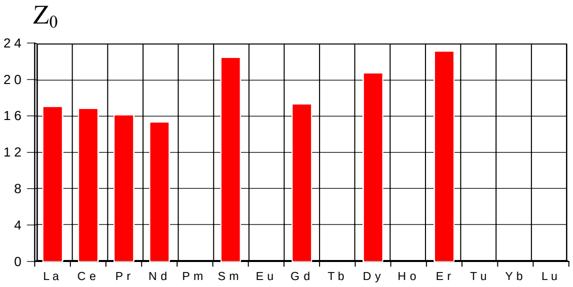


Fig. 8. **Hydration numbers Z_0 for lanthanide nitrate solutions at 20° C across the series**

As a consequence, the surface change density on the lanthanide ion increases from La to Lu, and this should give rise to an increase in the extent of the ion-dipole interactions between the Ln^{3+} and water molecules around the lanthanide ions. The primary hydration sphere number for the lighter ions (La^{3+} - Nd^{3+}) is nine, and the heavier ions (Gd^{3+} - Lu^{3+}) are predominantly eight-coordinate species. The ions Sm^{3+}-Eu^{3+} exist in equilibrium between nine-and eight-coordinate [52]. Our results also show a change of the hydration number in the lanthanide series: e.g. from La to Nd the hydration numbers are almost constant and in Gd-Lu range the hydration number increases. These results indicate that the increase in the number of water molecules affected by the increasing electric field of the cation exceeds the decrease of the amount of the coordinated water molecules. The inner-sphere hydration number change is probably the main factor explaining the discontinuity (the so-called ”gadolinium break”) observed in the middle of the series (in fact, the break occurs at Sm^{3+}, Eu^{3+} or Gd^{3+}, depending which property is examined) [58].

Our ultrasonic studies on the hydration of lanthanum salts indicate the hydration number of lanthanum nitrate is lower than those obtained for chloride [56, 59] and bromide [57] solutions which is due to the formation of inner sphere complexes by nitrate anion.

Measurements in medical-biological fluids

Synovial fluid

On the basis of ultrasound velocity measurements a cycle of investigations in synovial fluids was carried out and a method of detecting inflamed and degenerative diseases was found [60]. Precise absolute measurements were provided with a compact version of interferometer operating up to 50 MHz and equipped with a 2 ml chamber.

Synovial fluid is a highly viscous plasma – fluid excreted by cells that line the joint. One of its functions is to aid in lubrication of the joint. In the healthy joint synovial fliud lubrication does an excellent job of protecting the cartilage from wear. However in the diseased joint, synovial fluid become less viscous and therefore less effective in lubrication. The ultrasound velocity in synovial liquid at room temperature before and after injection of 0.1 % hyaluranidase was measured in order to improve the accuracy of joint disease diagnostics. Osteoarthrosis is diagnosed when the ultrasound propagation velocity before injection of hyaluranidose is 1514±0.6 m/s and 1507±0.3 m/s after injection. Arthritis is diagnosed at ultrasound velocities 1500÷1503 m/s and 1499÷1501 m/s respectively. In the course of four-week treatment the changes of the synovial fluid in rheumatic fever diseases have been studied [61]. It was found that ultrasound velocity in the synovial media of patients with rheumatic arthritis increases considerably, while in those with osteoarthrosis varies slowly. This observation is in agreement to synovial fluid viscosity measurements [62, 63] because diseases can be differentiated by measuring the viscosity of synovial fluid (rheumatoid arthrits<osteoarthritis<normal). Investigations of substances injected into joints in rheumatic diseases were carried out also. Solutions of polyvinilpyrolinone various concentrations and molecular mass according to their viscosity behaviour corresponding to requirement of artificial synovial liquid were investigated. These data are presented in the Table 6.

Table 6. **Ultrasound and viscosity parameters of some drugs injected into the joints at temperature 36.6° C**

Solution	Ultrasound velocity *c*, m/s	Adiabatic compressibility $\beta \times 10^{11}$, m^2/N	Relative viscosity η
Distilled water	1522.9	43.41	1
Dimethyl sulphoxide	1469.0	45.58	2.3
5 % PVP* of molecular mass 85 000	1540.9	42.09	3.7
10 % PVP* (M 65 000)	1560.7	40.54	7.6
15 % PVP* (M 8000)	1583.9	39.02	2.9
20 % PVP* (M 12 000)	1603.7	37.60	6.6
Dimethyl sulphoxide +15 % PVP*	1631.4	36.23	9.1

PVP* polyvinilpyrolidone

The conclusion can be drawn that a medical preparation produced of aqueous solution of polyvinilpyrolidone 15 % and dimethyl sulphoxide (volume relation 7:1) has the best rheological properties.

Cerebrospinal fluid

Cerebrospinal fluid (CSF) is a biologic fluid that occupies the subarachnoid space and the ventricular system around and inside the brain. Essentially, the brain ‘floats” in it. CSF is produced at a rate of 0.2-0.7 ml per minute or 600-700 ml per day. Since the brain can only contain from 135-150 ml, large amounts are drained primarily into the blood through arachnoid granulations in the superior sagittal sinus. This continuous flow into the venous system dilutes the concentration of larger, lipoinsoluble molecules penetrating the brain and CSF [64]. The composition of CSF is the following: low-molecular-weight proteins, glucose, lactate, cellular components, antigens, and microbial organisms. The CSF protein concentration is one of the most sensitive indicators of pathology within the central nervous system. The CSF total protein count may be helpful in diagnosing tumors, infection polyneuritis, vasculitis, blood in the CSF, and trauma. When the protein level decreases, it can indicate rapid CSF production. We investigated the CSF of 72 patients with various pathology of the central nervous system [65]. Fig. 9 shows as an illustration, dependence of the ultrasound velocity against the CSF total protein concentration at 36.6^o C for patients with the brain tumors. For one patient CSF was examined three times during the medical treatment and it was defined that the total protein concentration changes in the interval 1.01÷1.39 g/l and the ultrasound velocity 1534.2÷1534.8 accordingly. From the literature data [66] the normal value CSF protein is to 0.45 g/l and the average value of patients with brain tumors is 1.15 g/l, but the range may be 0.15÷19.2 g/l.

So, CSF total protein count may be helpful in diagnosing tumors but must be interpreted in the context of clinical findings and results of other laboratory tests.

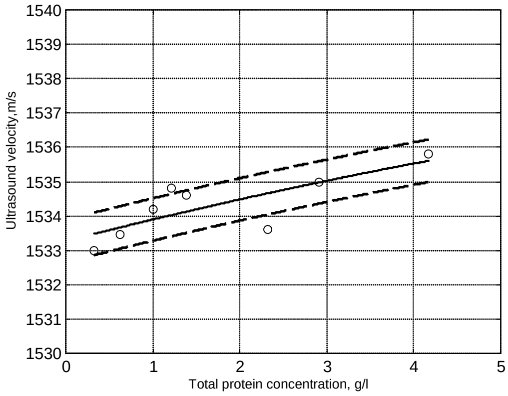


Fig. 9. **Experimental results of ultrasound velocity against the CSF total protein concentration for the patients with the brain tumors along with the probable dependence (solid line) and the dissipation field (dashed lines)**

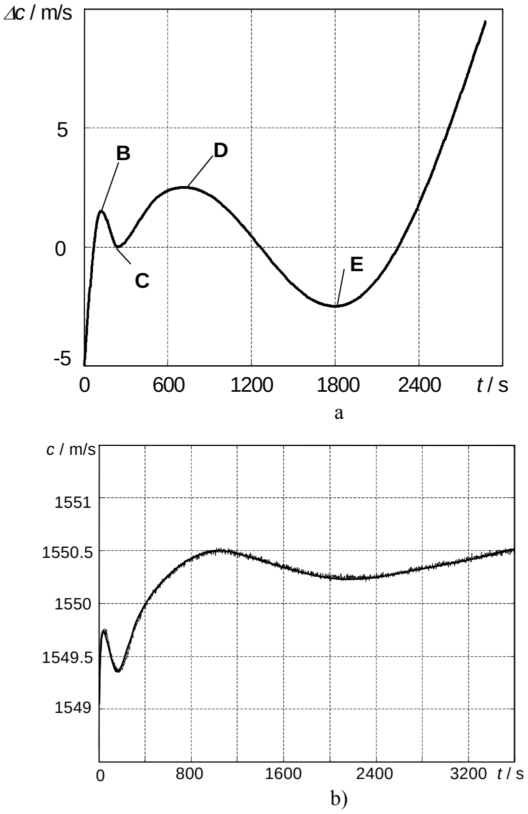
Study of blood coagulation and its phantom

Blood represents one of the most complex biochemical systems in living organism. Various components play integral roles in several life functions. Numerous studies have been carried out to acquire a more understanding of the properties of the blood coagulation process and increase the capability to diagnose various diseases. Ultrasonic methods for investigation of whole blood coagulation are based on different principles: spectroscopy [33, 67], measurement of velocity [34, 36, 39, 68], attenuation [69], impedance [70] or scattering in whole blood [71]. The interest in blood clotting ultrasonic monitoring increased during last years [72-76]. Measurements of ultrasound velocity variations reveal the main stages of the blood clotting [68]. However it was noticed that ultrasonic data depend on the measurement chamber inclination to the horizon. A random nature of this process was a problem to get a precise dynamic picture of the entire process. In order to reveal regularities of a blood clotting both in the time and space domains a novel investigation method was created, say multi-channel ultrasonic method which enables to measure ultrasound velocity variations simultaneously in a few parallel channels thus enabling to monitor blood clotting process in different but closely located spatial domains [38]. Some small volume different geometry chambers operating in a pulse-echo mode with a number of separate transducers or with a linear array were developed. Numerous investigations revealed the fact, that ultrasonic results may strongly depend on the transducers orientation. An optimal wave propagation direction and array orientation with respect to the gravitation vector was found, which gives the best information about the structure variation in different sections of the medium [40].

Fig. 10a present peculiar stages of blood coagulation curve of healthy person characterized by their duration and intensities, i.e. ultrasound velocity changes [37]. The curve is distinctive for one and multi-channel approaches. Points B and D mark the beginning and the end of blood clotting, at point C ultrasound velocity minimum is observed frequently. Interval DE represents so called latent refraction after which main retraction and lysis take place. The most informative for diagnostic purposes is the blood clotting process B-C-D.

For the purposes of dynamic calibration of blood coagulometer [68] we proposed to use free-radical chain polymerization reaction of acrylamide. Depending on composition it can be very similar to the blood clotting in the interval B-D from the point of view of ultrasound velocity variations. Twenty experiments were carried out with the optimal composition of acrylamide compound mixture [37]. This compound mixture is presented in the Table 7.

The mean acrylamide polymerization curve averaged from 20 identical experiments is shown in Fig. 10b. It represents clearly the main phases, typical for whole blood coagulation process and shows the ability of coagulometer to register fast ultrasound velocity variations. Thus, it can be used in blood clotting experiments as a reference medium.



a

b)

Fig.10. **Blood coagulation (a) and acrylamide polymerization (b) curves are similar in ultrasonic experiments**

Table 7. **Composition of acrylamide polymerization compound**

Materials	Formula	Concentration
Acrylamide	$CH_2{=}CHNH_2$	7 % on mixture weigh
Potassium persulphate	$K_2S_2O_8$	0.04 moles/litre
Sodium thiosulphate pentahydrate	$Na_2S_2O_3 \times 5H_2O$	1×10^{-4} moles/litre.
Distilled water	H_2O	Laboratory grade

The similar polymerization reaction was investigated in the multi-channel chamber. It was orientated as shown in Fig. 2, so the maximally different influence of gravitation on the reaction course was observed in different horizontal layers of the medium, corresponding to the array transducers.

Ultrasonic wave propagation is sensitive to growing of polymer macromolecular chains. The length of the chain reaction depends on the ratio of amount of active particles that are generated in time unit to numbers of these particles, which are produced for growing radical.

At the beginning of the polymerization (Fig. 11) dependence of the ultrasound velocity is almost identical in all channels, but later after 5 min the difference is very evident. In the upper part of the chamber amount of small and light species capable of initiating the polymerization is very large here. The ultrasound velocity decreases rapidly. In the channels from 2 to 4 the quantity of small species gradually decreases, changing the polymerization course. It is reflected on ultrasonic data. Curves minimums in time and ultrasound velocity values at the end of reaction vary gradually from channel to channel. At horizontal chamber orientation the gravitation influence in all channels is similar, and nearly identical courses of reaction is observed.

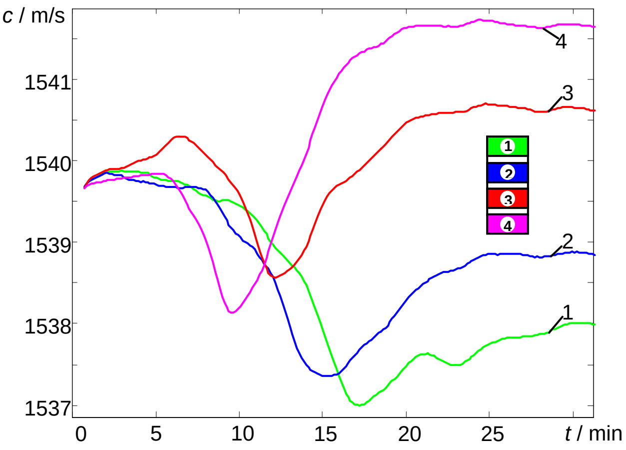


Fig. 11. **Acrylamide polymerization course as observed by vertically positioned four-channel chamber**

It is essential, that in multi-channel approach conclusions made for acrylamide polymerization are valid for blood coagulation.

Reference medium

Most popular reference liquid for the calibration of ultrasonic meters is distilled degassed water. In these measurements it is essential to check strictly the temperature, since a change in temperature by 0.01°C results in the change of ultrasound velocity in the water by 3 cm/s. So, we attempted to create mixtures having minimum temperature velocity coefficient. For this purpose aqueous mixtures of ethylene glycol, diethylene glycol, polyethylene glycol of molecule masses 300 and 400 were investigated [77-79]. The measurements have shown that ultrasound velocity in the interval of 10°C changes only by a few hundredths of a per cent in the mixture consisting of 66 % water and 34 % ethylene glycol. At 20°C, 25°C and 30°C respectively we obtained ultrasound velocity c_{20}=1648.22 m/s, c_{25}=1648.40 m/s and c_{30}=1648.00 m/s. Water-ethylene glycol mixtures of such composition can be regarded as standard ones. By varying the amount of ethylene glycol in the water-ethylene glycol mixture, ultrasound velocity can be changed from 1450 m/s to 1700 m/s; such values of ultrasound velocity are typical of biological liquids and soft tissues [80].

The studies of other aqueous glycol solutions showed that there exists such a characteristic concentration C_x at which ultrasound velocity and adiabatic compressibility do not depend practically on temperature in a certain interval. The values of ultrasound velocity and compressibility at these concentrations are given in Table 8.

Table 8. **Parameters of water-glycols mixtures with stable ultrasound velocity**

Glycoles	Concentration C_x, %	Ultrasound velocity c, m/s	Adiabatic compressibility $\beta \times 10^{11}$, m^2/N	Temperature interval ΔT_x, °C
ethylene glycol	35	1644	35.5	15÷35
diethylene glycol	31	1641	35.2	15÷40
polyethylene glycol-300	28	1650	34.5	15÷35
polyethylene glycol-400	27	1647	34.8	15÷35

Thus, water-glycols mixtures of such compositions can be used as standard samples for certifying ultrasonic measuring instruments.

Investigation for some technological processes

We want to mention here three directions of investigations:

- ultrasonic measurements in $FeSO_4$ water solutions with the 0.5% H_2SO_4 supplement in order to develop their concentration determination method in the technological process of metal factory,
- investigation of solutions for etching of iron with the aim of their quality control,
- ultrasound velocity measurements in petrol samples and the development of octane number determination method.

***Concentration determination of* $FeSO_4$+ 0.5% H_2SO_4**

During the technological process the concentration of $FeSO_4$ in solution may vary in the 190-210 g/l limits; 0.5% H_2SO_4 is added to these solutions. Dependencies of ultrasound velocity on temperature were determined in these systems using interferometric method (Fig.12).

Experimental values of the ultrasound velocity c (m/s) as a functions of temperature for three different concentrations (190 g/l, 200 g/l and 210 g/l) were described by polynoms consequently:

$$c_1=1590.83+4.046t-0.067t^2+3.8\times10^{-4}t^3, \quad (5a)$$

$$c_2=1599.34+4.506t-0.086t^2+5.9\times10^{-4}t^3, \quad (5b)$$

$$c_3=1607.28+5.024t-0.108t^2+8.4\times10^{-4}t^3, \quad (5c)$$

where t is the temperature of solutions.

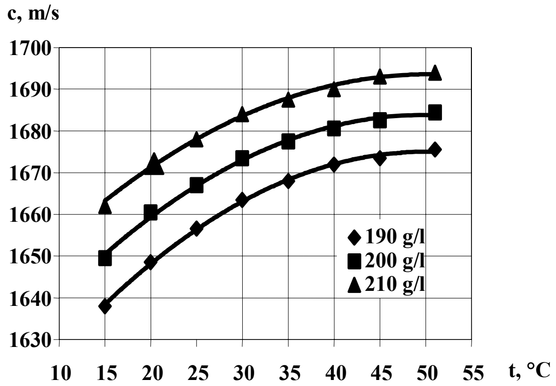


Fig.12. **Ultrasound velocity dependencies on temperature and concentration in $FeSO_4$ supplement**

The microprocessor based concentration meter was developed for the operation in factory conditions. Transducer unit (transmitter/receiver, distance 50 mm) is made fully of stainless steel as the medium is highly aggressive. In the temperature interval 15÷50° C concentration readings doesn`t depend on temperature and are stable within ±1 g/l.

Iron etching solutions

The main component of iron etching solution is 15% HCl acid. During the etching two associated processes are going in the solution – the decrease of HCl concentration and the increase quantity of Fe as $FeCl_3$ forms. For the investigation of the process ultrasound velocity concentration dependencies were determined at 30°C (Fig. 13).

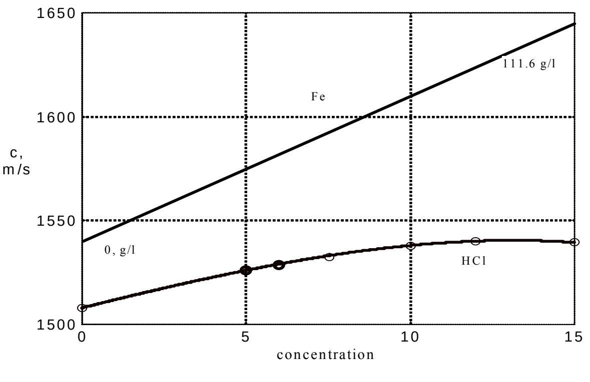


Fig. 13. **Ultrasound velocity dependencies in etching solution**

Ultrasound velocity in HCl water solutions increases in the interval 0÷15% approximately 30 m/s, but the main increase is observed up to 10%. $FeCl_3$ solutions were made adding $FeCl_3$ salt into 15% HCl. So, the beginning of the $FeCl_3$ dependence is observed at the same ultrasound velocity as 15% HCl. In the concentration interval of Fe in $FeCl_3$ 0÷111.6 g/l ultrasound velocity increases approximately 110 m/s and is linear as for all chlorides.

Thus the increase of velocity is 1 m/s per 1 g/l of Fe. The most interesting interval is 10÷15% of HCl. Here ultrasound velocity changes are very small. The influence of FeCl3 on ultrasound velocity is huge.

The necessary addition of concentrated HCl for the correction of etching solution can be determined according the velocity deviation from 1540 m/s, which is proportional to the quantity of Fe and thus the decrease of HCl concentration.

Octane number of petrol

In Europe Research Method is traditionally used for the determination of octane number of petrol. It is based on comparing the performance of the petrol being tested with the performance of a mixture of iso-octane and normal heptane. The experiments are provided in an engine under controlled conditions until a standard level of knock occurs. The octane number is the percentage of iso-octane in that mixture whose performance is the same as that of petrol under test [81]

So, a standard procedure is tedious and long lasting. We made an attempt to determine octane number of petrol on the basis of ultrasound velocity measurements, which are simple and fast. Petrol of different octane numbers (92, 95, 98) are produced from the same oil as a result of different degree of distillation and thus must be characterised with different acoustic properties. Indeed, we determined that ultrasound velocity increases as the octane number grows. The velocity difference $c_{98} - c_{92}$ is about 12 m/s. It depends a little on the oil source. The dependence ultrasound velocity=φ(octane number) is stable only in the case of distillation technology. If unknown increments are added in order to raise the octane number, dependencies are muddled. Thus, the ultrasonic method for the octane number determination best of all can be used in oil refinery.

There are some experimental features. If the petrol is placed in an open container, especially small, it evaporates rapidly and each successive ultrasound velocity measurement result is different. During the 10 minutes velocity increases about 7 m/s. So, the measurement chamber must be closed. The velocity value is about 1200 m/s depending on temperature and octane number. The second disturbing factor is a strong ultrasound velocity dependence on the temperature: -4.2 m/(s×deg). So its influence must be eliminated credibly. For that purpose we used a differential approach with two highly identical chambers (L=25 mm) and measurement channels. One chamber was filled with a certified reference ”92” petrol, the other- with tested. Both chambers were at the same temperature, and the velocity difference reflected only the octane number difference. The petrol quality measurement device is microprocessor based and the display shows directly octane number of the petrol with resolution of 0.1. Experiments revealed the effectiveness of differential approach as the readings of the given sample within ±0.1 are not depending on the surrounding temperature.

The apparatus was tested in various institutions in Lithuania, including oil refinery. The results were successful if the unknown increments were not used, which disturbed the correlation between ultrasound velocity and the structure of the petrol sample.

Conclusions

A survey of authors` scientific investigations in the field ultrasound velocity measurements in electrolyte solutions and various liquid systems is presented.

The main experiments were provided with a specially design ultrasonic laser interferometer within the frequency range 3÷200 MHz. Measurements in water were made up to 1250 MHz. Ultrasound velocity dispersion which is notoriously small (0.02÷0.3%) was investigated in the solutions of lanthanide salts. From the dispersion data relaxation parameters were extracted. The structural properties of solutions were determined, such as kinetic parameters for the formation of inner sphere complexes. Hydration phenomenon was investigated across the lanthanide series in order to explain non-monotonous variation of relaxation parameters.

Ultrasound velocity measurements were provided in the synovial and cerebrospinal fluids in order to improve disease diagnostics. Some correlations were found.

The pulse-echo method was employed in a miniature chamber for blood coagulation studies. The method revealed high sensitivity, especially in a multi-channel approach. The blood clotting phantom was created on the base of acrylamide polymerization reaction and was investigated. Experimental observations made for the acrylamide polymerization proved valid for blood coagulation, especially concerning of the gravitation influence on the course of clotting/polymerization process in different layers of the media.

The reference medium based on glycol/water mixtures was created, in which ultrasound velocity practically doesn`t depend on the temperature in the 15÷35^{o}C interval.

Some measurements were provided for the investigation of technological processes with the aim of concentration determination. A successful attempt was made for the determination of octane number of petrol on the base of ultrasound velocity measurements.

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B. Voleišienė, A. Voleišis

Ultragarso greičio matavimai skysčiuose

Reziumė

Apžvelgiami autorių atlikti išsamūs ultragarso greičio matavimai elektrolitų tirpaluose ir įvairiose skystosiose terpėse.

Ultragarso greičio dispersijos matavimai lantanidų druskų vandeniniuose tirpaluose atlikti esant 3-200 MHz dažniui specialiai šiam tikslui sukurtu ultragarsiniu lazeriniu interferometru. Dispersijos vertė tesiekia 0,02÷0,3 % ultragarso greičio vertės, todėl šiems matavimams atlikti buvo būtinas didelis tikslumas. Iš dispersijos duomenų nustatyti relaksaciniai parametrai, jų priklausomybė nuo koncentracijos ir temperatūros. Apskaičiuoti greitų cheminių reakcijų, vykstančių tirpaluose, kinetiniai parametrai. Relaksacinių parametrų nemonotoninis kitimas lantanidų eilėje aiškinamas skirtinga šių jonų hidratacija. Ligos diagnostikos tikslu atlikti ultragarso greičio matavimai sinoviniame sąnarių ir smegenų skysčiuose. Nustatytos tam tikros koreliacijos. Impulsiniu metodu miniatiūrinėje kiuvetėje tyrinėtas ultragarso greičio kitimas kraujo krešėjimo ir akrilamido polimerizacijos metu, aptiktas procesų eigos identiškumas. Daugiakanalėje kiuvetėje tyrinėta gravitacijos įtaka šiems procesams, nustatyti dėsningumai. Glikolių vandeninių tirpalų pagrindu ultragarsiniams matuokliams sukurta etaloninė terpė, kurioje ultragarso greitis nepriklauso nuo temperatūros. Tyrinėti metalo pramonės įmonių technologiniame procese naudojami cheminiai tirpalai ir jų koncentracijos ultragarsinio nustatymo galimybės Sukurtas metodas, kuris leidžia iš ultragarso greičio duomenų nustatyti benzino oktaninį skaičių.

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