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A Summary and an Index of Work Completed Under the Task NR. 051-162 and NR. 384-305

by

M.A. Barrett-Gültepe, M.E. Gültepe and E. Yeager

February 25, 1982

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I. Introduction

This is the summary report for work done under the general title (Ultrasonic Waves and Electrochemistry), task numbers 051-162 and 384-305. During the years October 1, 1948 to December 31, 1981. Starting January 1953, the task number was changed to 384-305 and continued until December 31, 1981.

The work done under the title "Ultrasonic Waves and Electrochemistry" can be divided into five main groups:

- The use of ultrasonic waves as a tool in the study of electrolytic solutions, hydrated ionic melts and electrochemical interfaces.
- Ultrasonic study of colloidal dispersions and sediments in electrolytic solutions.
- Promotion of chemical and electrochemical effects by ultrasonic waves.

In Appendix A the list of publications produced under the contract research is given and references cited in the following text refer to this list. In Appendix B the list of technical reports prepared under the task numbers NR. 051-162 and NR. 384-305 is given. Finally, in Appendix C, a list of the accomplishments of the work sponsored by these two task numbers and the significance of these results to the Navy and Physical Acoustics are given.

II. The use of ultrasonic waves as a tool in the study of electrolytic solutions, hydrated ionic melts and electrochemical interfaces

When acoustical waves are propagated through an electrolyte solution, small a.c. poltentials are generated between points separated by a phase distance other than a multiple of one half the wavelength. These a.c. potentials were predicted on theoretical grounds by Peter Debye in 1933 but not experimentally found until 1948 in work at this university^{2,4} (Technical Report No. ?).

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The effect occurs principally because of differences in the dynamic reaction of the cations and anions to the sound field (inertial and pressure gradient effects). Subsequent theoretical work as part of the ONR research has shown that the effect provides a measure of the partial molal volumes of the individual ions and hence ion solvent interactions.

This effect (originally called the Debye effect but more recently ionic vibration potential) was originally detected using inert electrodes in the electrolyte and a standing wave technique to differentiate between the true effect and cross talk (electromagnetic coupling). In the 1960's much further work was done on the effect using pulse modulated ultrasonic waves and the much slower propagation time of the sound waves compared to the speed of light to differentiate between the true effect and crosstalk. The pulse technique facilitated quite quantitative measurements of the small potentials [\circ lµV per unit velocity amplitude (1 cm/s)] and yielded the most reliable value for the individual partial molal volumes now available [see Technical Report No. 45]. The measurement of the effect has been carried out not only in a large number of electrolytes but also in polyelectrolytes and micelle systems. Its usefulness has proved far greater than ever invisioned by Debye.

The first systematic and quantitative studies of ionic vibration potential were performed only in 1966. The use of a double probe assembly partially immersed in the solution under investigation^{32,36} provided the experimental verification of several predictions of the most thorough theoretical treatment of the ionic vibration potential, given in 1947.¹ On the other hand, a closer examination of the physical meaning of the apparent molar masses of the solvated ions which appear in this treatment indicated that the ionic vibration potential is closely related to a weighted difference between the partial molal volumes of the ions present in the system.^{32,36}

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It thus became possible by combining the value of the ionic vibration potential for a given electrolyte in a given solvent, and the partial molal volume at infinite dilution for the same electrolyte in the same solvent to obtain the values of the partial molal volumes of the individual ions constituting this electrolyte. This was done between 1966 and 1968 for a series of electrolytes of widely differing nature in aqueous solutions. 36, 39, 40, 42

In addition to ionic vibration potential, the first detection and preliminary measurements of polyelectrolyte vibration potential were made in this laboratory in 1962.²⁶ With the development of the sophisticated apparatus made for ionic vibration potential measurements, quantitative measurements of polyelectrolyte vibration potential with accuracies of \pm 5% are reported in Technical Report No. 30 from this study. The following conclusions were reached:

- Polyelectrolyte vibration potentials depend on the nature, concentration, and percent neutralization of the polyelectrolyte as well as on the nature of the gegenion and on the nature and concentration of any added salt.
- 2. The experimental results are in quantitative agreement with theory based on the ionic vibration potential mechanism and the polymer bead model.
- 3. The polyelectrolyte vibration potential can be used to determine the partial molal volume of a monomer unit in the polymer bead model. (The value is 45.6 cm³/mole for unneutralized polyacrylic acid.)

In Technical Report No. 31, the results were given for the ultrasonic vibration potential measurements in tetra alkylammonium halides at 220 kHz. The experimental and theoretically predicted values were in good agreement at low concentrations.³⁹ The concentration dependence can be explained in

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terms of cation-cation pairs and ion triplets provided the volumes of these aggregates are much less than the sum of the volumes of the separate ions. A.C. potential components can also be generated at electrode-solution interfaces, particularly in dilute electrolytes.

An interesting electrokinetic effect¹² has been studied for the first time in our laboratory with pulse modulated ultrasonic waves (see Technical Report No. 5). If a wire with a fiber covering is placed in a dilute solution of an electrolyte and exposed to ultrasonic waves, a.c. potential differences are developed between the wire and the bulk of the surrounding solution. The dependence of this effect on solution parameters as well as the type of porous covering clearly indicates that the effect is associated with the diffuse layer of ions surrounding the fibers, and hence, is electrokinetic in nature. Quantitative measurements have been made at 200 kHz and the electro-acoustic response of the cotton covered copper wire in 1 x 10^{-4} M NaCl solution is 5 x 10^{-8} volts per dyne cm⁻². The frequency dependence of this effect was also studied and it was found that at 1 MHz, there was a decrease of approximately 10 dB in the electro-acoustic response. Besides its possible use as a velocity sensitive acoustical probe, it can be used to study electrokinetic effects involving fibers and porous coatings.

In addition to these electrokinetic effect studies, a.c. and d.c. streaming potential measurements were made with porous packings consisting of ion exchange resins, pyrex glass wool, nylon and surgical cotton in a large number of aqueous solutions. In contrast to d.c. streaming potential measurements, when the velocity of the liquid flow through the porous packing is sinusoidal, a.c. streaming potentials are produced between the opposite sides of the packing. Special apparatus was developed for the a.c. streaming potential measurements at frequencies up to 30 Hz. No frequency dependence was found over the limited frequency range involved in the present work. The dependence of

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the streaming potential on type and concentration of electrolyte solution is the same as would be predicted on the basis of established theories for conventional d.c. methods. The experimental results obtained by a.c. and d.c. streaming potential measurements are in complete agreement (see Technical Report No. 21).

If sound waves impinge on an electrode at which a gas is being liberated by electrolysis an alternating potential is produced on the electrode relative to the bulk of the surrounding solution. The amplitude of the socalled "alternating components in electrode potential" is dependent on the acoustical amplitude, the polarizing current density and the conductance of the solution, but is essentially independent of the base metal upon which the hydrogen gas is evolved. The acousto-electrochemical effect has been explained at ultrasonic frequencies in terms of the modulation of the i-r drop in the solution in the immediate vicinity of the electrode through periodic variations in the size of the gas bubbles found at the electrode surface.^{4,5} (See Technical Reports Nos. 3, 8, 9) It has been suggested that the "alternating components in the electrode potential" effect might be used in the form of an extremely small probe for the determination of phase and amplitude at ultrasonic frequencies, particularly above 100 kHz.

As we mentioned before, when ultrasonic wave impinge on an electrode immersed in electrolyte, various a.c. effects are produced. The converse of such effects is produced when an a.c. potential is applied to an electrochemical interface relative to the bulk electrolyte. Periodic volume changes are produced at the solution side of a metal-electrolyte interface. This in turn gives rise to the generation of sound waves of the same frequency in the solution phase. The Technical Report No. 44 describes the first detection of these sound waves using a gold electrode in an acid electrolyte. Preliminary measurements were reported as a function of d.c.

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(bias) electrode potential.^{55,56} It was also found that the effect was particularly sensitive to adsorbed species such as organics. This is not surprising since such species adsorb strongly on the electrode at various potentials and can also undergo faradiac processes yielding various oxidation and reduction products. This effect was found to be too small to be a practical source for sound generation. It is possible, however, to enhance the effect by stacking a number of very thin electrodes with very small electrolyte gaps. The main use of this effect, however, is the study of adsorbed species and anodic film formation on metal surfaces in electrolytes.

Ultrasonic absorption measurements provide a means for studying the kinetic parameters of processes which occur too rapidly to be studied by conventional techniques.²⁹ Specific processes such as unimolecular and dissociation reactions, proton-transfer reactions (e.g. hydrolysis or acid-base dissociation) can be studied by ultrasonic absorption and several other relaxation techniques. Investigations of relaxation times shorter than 10^{-6} s, are suitable for ultrasonic absorption measurements. During the contract research various apparatus were built to cover the range 0.03 to 550 MHz. A survey of some of the salient features of these are given in Table I. Details are given in Technical Report Nos. 32 and 35. The spherical resonator apparatus has more recently been updated to incorperate computer control allowing much more detailed measurements without undue expenditure of the experimenters time (see Technical Report No. 48).

A review of ultrasonic relaxation in electrolytic solutions is given in Technical Report No. 25. Ultrasonic relaxation was re-examined in $MgSO_4$ solutions in order to resolve discrepencies in published data.^{31,43} Two relaxation frequencies were found adequate to describe the data if the nonrelaxation absorption is treated as an adjustable parameter, in contrast to the 3 or 4 relaxation frequencies reported earlier by other groups (Technical

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Report Nos. 35 and 37). Further work done on some other 2:2 electrolytes (copper sulfate and cobalt sulfate) indicated that the high frequency absorption peak could be attributed to the diffusion controlled second order process leading to the formation of an encounter complex (see Technical Report No. 32).

In Technical Report No. 26 a study of the kinetics of the hydrolysis of the cyanide ion is described, using ultrasonic absorption measurements²⁸ over the frequency range 30 kHz to 25 MHz. A single relaxation frequency was observed which depends on concentration in a manner expected theoretically for the hydrolysis reaction. Similarly, a single relaxation was found⁴⁴ in acetic acid, agreeing with the calculations on the equilibrium and kinetic parameters for the ionization of acetic acid determined by other techniques. The data yielded values for k_{dissoc} , k_{assoc} and ΔV . The measurements of relaxation times for chemical processes slower than 10^{-5} s cannot be determined with accuracy by ultrasonic measurements. The lowest frequency obtainable by the 100-liter titanium spherical resonotor in use in our laboratory is 20 kHz.

Apparatus for pressure step and shock wave measurements were first developed⁴¹ as part of the ONR research (Technical Report No. 27) and used to measure the relaxation times extending from 10^{-7} to the half life of a graduate student in this university for various chemical processes involving ionic equilibria. The pressure step method involves the sudden release of an applied static pressure on an electrolytic solution. After the pressure release the re-establishment of equilibrium between free hydrated ions and associated species is followed by means of conductance measurements. Relaxation times longer than 50 µs can be measured with this apparatus. This method was applied to the study of complex formation between polyvalent cations and various ligands (Technical Report No. 35).

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Many of the more interesting association-dissociation processes involving transition metal complexes have relaxation times shorter than 50 μ s and hence cannot be studied with the above techniques. A much faster pressure rise can be accomplished by utilizing the non-linear properties of the transmitting liquid to sharpen up a shock front. The velocity of sound in a liquid increases with pressure and consequently the leading edge of a pressure pulse will steepen as the pulse is propagated through the liquid. In contrast, a dilitation pulse, such as is produced in the pressure step technique, will flatten out. The pressure-shock technique was demonstrated to be a relatively simple means for measurement of relaxation times for chemical processes in the range 10^{-6} to 10^{-3} . Details are given in Technical Report No. 33.

The low frequency relaxation in sea water, indicated by a long range sound propagation, was investigated using temperature-jump measurements⁴⁸ in which a hydrogen ion sensitive color indicator was added to permit optical readout. The measurements indicated a single relaxation at 1.5 x 10^{-4} s at 9.7°C originating form boron with the B(OH)₃ - B(OH)₄ as the likely relaxation process. This was the first time that equilibrium involving borateboric acid exhibited a relaxation frequency at \sim 1 kHz and was responsible for the corresponding relaxation sea waters.

Acoustic measurements are difficult above 550 MHz. In order to gain insight into relaxation phenomena above this range, it is necessary to employ optical techniques. Brillouin scattering studies on a number of electrolytes,^{50,52} including halides, nitrates and sulfates, yielded hypersonic velocity data from the frequency shift of the Brillouin components, and hypersonic absorption coefficients from the line widths. The results compare favorably with those from ultrasonic velocity and absorption data at lower frequencies. The ratio of the light intensity of the Rayleigh component to that of the Brillouin line

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was compared with theory, and agreement was found for solutions of alkali halides and alkali earth halides and nitrates, confirming simple concentration fluctua⁺ion theory. However, solutions of 2:2 sulfates gave intensity ratios significantly higher than theory. Brillouin scattering and ultrasonic measurements were both utilized to investigate the high frequency (5 MHz to 12 GHz) relaxations of zinc nitrate and calcium nitrate hydrate melts. A distribution of relaxation times was observed. These high frequency studies are given in Technical Report No. 40, 41 and 43.

III. <u>Ultrasonic study of colloidal dispersions and sediments in electrolytic</u> <u>solutions</u>

When sound waves are propagated through a colloidal suspension in an electrolyte, much larger a.c. potentials are generated than just in an electrolyte. This effect also occurs because of differences between the displacement of the colloidal particle and the ions of the system. Each charged colloidal particle is surrounded by an ionic atmosphere or diffuse ionic cloud which is normally symmetrical. In the presence of the sound waves this ionic atmosphere is periodically distorted, giving rise to periodic oscillating dipoles. This in turn results in "colloidal vibration potential". This much larger effect was first detected by A.J. Rutgers in 1938. Quantitative studies of the effect have also been carried out as part of the ONR research. The effect is a powerful tool for checking the theoretical models for charge distribution about colloidal particles. This is intrinsic to the electrolyte and colloid-electrolyte media through which the sound waves are propagated.

Measurements on colloidal vibration potential were made in colloidal silica suspensions at frequencies from 200 kHz to 1.2 MHz as a function of

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particle size, colloidal concentration and ionic strength. In this work, corrections have been made for the electrical loading effects of the measuring equipment for suspensions of very low conductances. Quantitative colloidal vibration potentials in silica suspensions were measured in 1960 an the results were presented in Technical Report No. 23. The experimental values for the colloidal vibration potential are in reasonably good agreement with values calculated from the treatment of this effect by Enderby, particularly for suspensions of relatively high specific conductance.

Ultrasonic vibration potential measurements were also made in solutions of salts exhibiting micelle formation. Experimental data indicated that in dilute solutions of sodium lauryl sulfate at concentrations far below the critical micelle concentration, the vibration potentials agree well with the theoretical values. The concentration dependence of the vibration potential in various micelle solutions show that at concentrations below the critical micelle concentration there is strong evidence for the formation of charged aggregates which were representing the neuclei for micelles. Ultrasonic vibration potential can be used to determine the critical micelle conentration.

The propagation of sound in concentrated colloidal dispersions and marine sediments was theoretically and experimentally studied with particular attention to the influence of interfacial phenomena. The following model colloid systems were chosen: kaoline, montmorillonite, polystyrene latex particles and PVA (polyvinylacetate-polyvinylalcohol block co-polymer). For the first time, the effect of hetero-deflocculation of two dissimilar mineral grains on the velocity of sound was established in concentrated dispersions in the of kaoline and montmorrilonite mixtures (see Technical Report No. 46).

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It had been shown in earlier work on polystyrene latex dispersions by M.A. Barrett Gultepe, D.H. Everett and M.E. Gultepe that acoustic absorption in the dispersions is strongly influenced by the nature of the electrolyteparticle interface, and that an adsorbed layer of PVA considerably alters the acoustic absorption properties. Sound velocity measurements made in this laboratory on a similar system as a function of temperature yielded compressibility values for the PVA covered latex that differed from that expected from the simple additivity effect of the two components. At low temperatures the low compressibility found may be due to the hydrophobic interaction between acetate groups and the polymer backbone (Technical Report in preparation).

Ultrasonic waves have also proved useful in producing emulsion.³⁴ This phenomena was studied in our laboratory using electron microscopy to examine the particle size distribution with freeze type techniques. A surprising result is that the particle distribution has certain narrow ranges of size completely missing. These size droplets are apparently unstable in the sound field and depend on the frequency. Attempts to predict such instabilities on the basis of surface wave models, however, were not fully successful. Furthermore, some of the missing sizes corresponded to subharmonics.³⁴

IV. Promotion of chemical and electrochemical effects by ultrasonic waves

Electrodeposition of copper experiments in the presence of ultrasonic waves at 200 kHz and 1 MHz at 1 watt cm^{-2} were made in our laboratory (see Technical Report No. 10). The schlierer technique was used to examine the concentration gradients at the cathode and anode during the electrodeposition of copper. The ultrasonic waves seem to remove completely these concentration

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gradients at reasonable current densities. The deposition of copper, as involved in the above study, however, is characterized by low activation polarization and negligible simultaneous hydrogen evolution. In Technical Report No. 15 the effects of ultrasonic waves on the structure of the electrodeposited nickel during the hydrogen evolution were reported. X-ray diffraction studies of the deposits indicate that the ultrasonic waves decrease the tendency for the 110 planes of the face centered cubic system to be oriented parallel to the electrode surface at high current densities and increase the tendency for the 100 planes to be oriented parallel to the surface at low current densities.

All the contract research done on the subject of the effects of ultrasonic waves on the electrodeposition of metals lead to the conclusion that the ultrasonic effects are generally an extension of what is encountered with increased agitation of a more conventional nature. Ultrasonically produced cavitation is therefore one of the most effective ways of promoting mass transport to and from solid-liquid interfaces.

When high intensity sound waves propagate through liquids, chemical reactions often occur within the liquid. Without exception, these chemical changes are the result of either acoustically produced cavitation or the progressive heating of the liquid through the absorption of the acoustical energy within the liquid. In Technical Report No. 17 an attempt was made to obtain information concerning the mechanism for sonochemical formation of hydrogen peroxide in oxygen saturated solutions by an isotopic tracer technique involving 0^{18} . The experimental results indicated that in oxygen saturated solutions the 0-0 bond of the oxygen molecule is not formally broken during cavitation even at intensities of 100 watts/cm². In water saturated with oxygen at atmospheric pressure, approximately one-third of the peroxide oxygen is

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TABLE I. Ultrasonic Absorption Apparatus Constructed and Used from 0.03 to 550 MHz.

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Type of apparatus	Ultrasonic principle or modification	f (MHz)	Path (cm)	Volume (1.)
Resonator	radial mode reverberation in spherical resonator; computer controlled	0.02-0.3	ł	12,50,100
Resonator	radial and axial mode in cylindrical resonator; computer controlled	.01503		.25
Reverberation	wid e -band noise (statistical) reverberation	0.2-1	l 1	e
Carstensen HF send-receive	pulse technique; fixed transducer distance of 66 cm with variable solution/solvent path length to minimize diffraction effects; impedance match- ing; comparison method	0.7-14	66	59
VHF pulse echo	ultrasonic cell modification of apparatus to permit transducer-reflector alignment; pulse technique; variable path length; attenuator method; (attenuator matching devices)	5-65	20	0.035
VHP send-receive	modification of pulse echo to send-receive; pulse technique; send and receive transducers; ultra- sonic attenuation measured with a comparison signal generator; prototype for HF and UHF systems impednace matching; diffraction loss correction	2-95	01	0.14
UHF send-receive	pulse techníque; send-receive transducers on fused quartz delay línes; síngle trackíng oscillator; impedance matching; comparison method	100-550	-	0.002

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derived from oxygen gas and the remainder from the water. In 30% methanolwater solutions saturated with oxygen gas, all of the peroxide oxygen originates with the molecular oxygen and none from the water or methanol.

In contrast to sound wave induced chemical reactions in solutions, the degradation of polymers by ultrasonic waves can be explained by mechanical effects rather than thermal or chemical effects. In Technical Report No. 18 the rate of degradation of polystyrene in organic solvents by ultrasonic waves has been studied. It was concluded that degradation does not occur in the absence of cavitation even at acoustical intensities as high as 1000 watts/ $\rm cm^2$. The extreme rates of shear in the liquid adjacent to a resonating cavitation bubble are believed to be responsible for the mechanical degradation of the polymers and represent an interesting means for studying the extreme mechanical effects associated with cavitation.

V. Advances in acoustic instrumentation

The most recent development in our laboratory has been the introduction of computers for controlling the acoustic measurements. A microcomputer controlled velocity and absorption measurements system was developed for cylindrical and spherical resonators. The microcomputer initiates predetermined frequency steps with the aid of a programmable synthesizer, with the output amplified and applied to the driving crystal. The received signal is fed into a programmable tuned amplifier and demodulated. When the computer finds a long decaying resonance mode, decay rate measurements were made and stored in a floppy disk for later analysis. The system allows for very detailed mode mapping of the resonator by accumulating frequency-amplitude data, along with a recod of the temperature. The amplitude decay can be followed through 70 dB with reproducibility within ± 0.2 dB s⁻¹. With this instrumentation a better defined relaxation

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was obtained for 0.0041 M $MgSO_4$ (Technical Report No. 48).

In order to obtain better results below 50 kHz, a 100 liter titanium sphere, on loan from Woodshole Oceanographic Institute, is interfaced to the computerized instruments. Q values as high as a million were observed around 20 kHz when the sphere was filled with distilled water.

The spherical resonators are not suitable for concentrated dispersions due to the fact that their narrow openings for introducing and removing material causes some difficulties in handling the dispersions. For this reason cylindrical resonators were built of polycarbonate. Using the lower radial modes of one of the resonators, a Q value of 1500 was obtained around 18 kHz, compared to Q = 900 for similar resonators described in the literature. The better Q obtained in this work is probably due to the greater compliance of the polycarbonate material.

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APPENDIX A

References and Complete Publication List

- 1. "The Application of Ultrasonic Waves to the Study of Electrolytic Solutions: I. A Modification of Debye's Equation", J. Bugosh, E. Yeager and F. Hovorka, J. Chem. Phys. <u>15</u>, 592 (1947).
- 2. "II. The Detection of the Debye Effect", E. Yeager, J. Bugosh, F. Hovorka, and J. McCarthy, <u>ibid</u>: <u>17</u>, 411 (1949).
- 3. "III. The Effect of Acoustical Waves on the Hydrogen Electrode", E. Yeager and F. Hovorka, <u>ibid</u>. <u>17</u>, 417 (1949).
- "The Measurement of Ionic Vibration Potentials with Pulse-Modulated Ultrasonic Waves", E. Yeager, J. Bugosh, and F. Hovorka, Proc. Phys. Soc. (London) <u>64B</u>, 83 (1951).
- 5. "Electronic Instrumentation for Polarization Measurements", D. Staicopoulos, E. Yeager and F. Hovorka, J. Electrochem. Soc. <u>98</u>, 20 (1951).
- 6. "The Effect of Acoustical Radiations on the Hydrogen Electrode", E. Yeager and F. Hovorka, <u>ibid</u>. 98, 12 (1951); Discussions, ibid. 98, 510 (1951).
- 7. "The Applications of Ultrasonic Waves in Chemistry", E. Yeager, School of Science and Mathematics <u>21</u>, 133 (1952).
- 8. "Ultrasonics: Tool of the Chemist", E. Yeager and F. Hovorka, Research Reviews, <u>6</u>, 1 (1952).
- 9. "The Effect of Ultrasonic Waves on Hydrogen Overvoltage", E. Yeager, T. Oey and F. Hovorka, J. Phys. Chem. 57, 268 (1953).
- "Ultrasonic Waves and Electrochemistry. I. A Survey of Electrochemical Applications of Ultrasonic Waves", E. Yeager, H. Dietrick and F. Hovorka, J. Accoust. Soc. Am. <u>25</u>, 443 (1953).
- 11. "II. Colloidal and Ionic Vibration Potentials", E. Yeager, H. Dietrick and F. Hovorka, <u>ibid.</u> 25, 461 (1953).
- 12. "III. An Electrokinetic Effect Produced by Ultrasonic Waves", H. Dietrick, E. Yeager, J. Bugosh, and F. Hovorka, <u>ibid.</u> 25, 461 (1953).
- 13. "IV. The Production of Alternating Components in the Potential of a Polarized Hydrogen Electrode with Ultrasonic Waves", H. Dietrick, E. Yeager, J. Bugosh and F. Hovorka, ibid. 25, 466 (1953).
- "The Effect of Ultrasonic Waves on the Electrodeposition of Copper", W. Wolfe, H. Chessin, E. Yeager, and F. Hovorka, J. Electrochem. Soc. <u>101</u>, 590 (1954).
- 15. "Ultrasonics and Electrochemistry. V. The Frequency Characteristics of the Electrokinetic and the A. C. Polarized Gas Electrode Effects", F. Saunders, E. Yeager and F. Hovorka, J. Acoust. Soc. Am. 27, 410 (1955).

- 16. "Ultrasonics", E. Yeager and F. Hovorka, Encyclopedia of Chemical Technology, van Nostrand, 1955.
- 17. "Chemical Applications for Ultrasonic Waves", E. Yeager, J.Soc. Cos. Chem. <u>8</u>, 139 (1957).
- "Isotopic Techniques in the Study of the Sonochemical Formation of Hydrogen Peroxide", M. Del Duca, E. Yeager, M. Davies, and F. Hovorka, J. Accoust. Soc. Am. <u>30</u>, 301 (1958).
- "Quantative Measurements of Ionic Vibration Potentials", J. Booker, F. Hovorka and E. Yeager, Chapter 6 in Electrochem. Monograph, "The Structure of Electrolytic Solutions", edited by W. Hamer, John Wiley and Sons, Inc., 1959.
- 20. "Ultrasonic Vibration Potentials in Non-Ionic Liquids", E. Yeager, J. Booker and F. Hovorka, Proc. Phys. Soc. (London) <u>73</u>, 690 (1959).
- 21. "Effect of Ultrasonic Waves on Concentration Gradients", R. Penn, E. Yeager and F. Hovorka, J. Acoust. Soc. Am. 31, 1372 (1959).
- 22. "A Relaxation Method for the Study of Electrode Processes", E. Yeager, Z. Elektrochem. 64, 86 (1960).
- 23. "Acousto-Electrochemical Effects in Electrode Systems", E. Yeager, Transactions of the Symposium on Electrode Processes, E. Yeager (editor), John Wiley and Sons, 1961.
- 24. "Surface Wave Phenomena During Ultrasonic Emulsification", E. Yeager, A. Patsis, and F. Hovorka in "Proceedings on the Third International Congress on Acoustics", L. Cremer (editor), Elsevier Publishing Co., 1961, pp. 1276-9.
- 25. "Ultrasonic Absorption in Toluene", E. Yeager and G. Verma, <u>ibid</u>, pp. 559-62, 1961.
- 26. "Ultrasonic Vibration Potentials in Solutions in Polyelectrolytes", E. Yeager, J. Booker, and F. Hovorka, in "Proceedings of the Fourth International Congress on Acoustics", Elsevier Publishing Co., 1962, pp. 45-9.
- 27. "Fundamental and Processing Applications for Sound Waves", E. Yeager, Proceedings Desalination Research Confrence, National Academy of Sciences-National Research Council, Publication 942, 1963, pp. 229-254.
- "Ultrasonic Investigation of the Rate of Hydrolysis of Potassium Cyanide", J. Stuehr, E. Yeager, T. Sachs and F. Hovorka, J. Chem. Phys. <u>38</u>, 587-593 (1963).
- 29. "The Propagation of Ultrasonic Waves in Electrolytic Solutions", E. Yeager and J. Stuehr, Chapter 6 in <u>Physical Acoustics</u>, Vol. 2A, W. Mason, editor, Academic Press, New York, 1965, pp. 351-462.
- 30. "Quantitative Studies of Ultrasonic Vibration Potentials", E. Yeager and R. Zana, Reports of the Fifth International Congress on Acoustics, Vol. 1A, D31 (1965).

-17-

- 31. "Ultrasonic Absorption in Manganese Sulfate Solutions", E. Yeager and L. Jackopin, J. Phys. Chem. <u>70</u>, 313 (1966).
- 32. "Determination of Ionic Partial Molal Volumes from Ionic Vibration Potentials", E. Yeager and R. Zana, J. Phys. Chem. <u>70</u>, 954 (1966).
- 33. "Studies of Relaxation Effects in Electrolytic Solutions with the Pressure-Step Method", H. Hoffmann, J. Stuehr and E. Yeager, Chapter 14, <u>Chemical</u> <u>Physics of Ionic Solutions</u>, B. Conway and R. Barradas, editors, J. Wiley and Sons, New York, 1966, pp. 255-293.
- 34. "Polyelectrolyte Vibration Potentials", R. Zana and E. Yeager, Polymer Letters 4B, 947-951 (1966).
- 35. "Hydrogen Overvoltage on Platinum", by F. Ludwig and E. Yeager in Electrode Processes, E. Yeager, H. Hoffmann and E. Eisenmann, eds., The Electrochemical Soc., Inc., New York, 1966, pp. 1109-1111.
- 36. "Ultrasonic Vibration Potentials and Their Use in the Determination of Ionic Partial Molal Volumes", R. Zana and E. Yeager, J. Phys. Chem. <u>71</u>, 521-536 (1967).
- 37. "Ultrasonic Absorption and Ion Association in Sodium Acetate Solutions", J. Stuehr and E. Yeager, J. Chem. Phys. <u>46</u>, 3, 1222-1223 (1967).
- 38. "Quantative Studies of Ultrasonic Vibration Potentials in Polyelectrolyte Solutions", R. Zana and E. Yeager, J. Phys. Chem. <u>71</u>, 3502-3516 (1967).
- "Ultrasonic Vibration Potentials in Tetraalkylammonium Halide Solutions", R. Zana and E. Yeager, J. Phys. Chem. <u>71</u>, 4241-4244 (1967).
- 40. "Potentiels de Vibration Ultrasonore dans les Solutions Aqueuses de Sels D'Acides Organiques", R. Zana and E. Yeager, J. Chim. Physique 65, 467 (1968).
- 41. "Pressure Shock Technique for the Study of Chemical Relaxation", H. Hoffmann and E. Yeager, Rev. Scient. Instr. <u>39</u>, 1151 (1968).
- 42. "Potentiels de vibration ultrasonore dans des solutions aqueuses d'amphiphiles", R. Zana and E. Yeager, J. Chim. Physique <u>66</u>, 252 (1969).
- 43. "Ultrasonic Relaxation in Manganese Sulfate Solutions", by LeRoy G. Jackopin and Ernest Yeager, J. Phys. Chem. <u>74</u>, 21, 3766-3772 (1970).
- 44. "Ultrasonic Relaxation in Aqueous Acetic Acid Solutions", L.G. Jackopin and E. Yeager, J. Acoust. Soc. Am. <u>52</u>, 831-836 (1972).
- 45. "Concentration Dependence of Ionic Vibration Potentials", by Earnest Yeager and Raoul Zana, J. Phys. Chem. <u>76</u>, 1086-7 (1972).
- 46. "Ultrasonic Relaxation in Calcium Nitrate Tetrahydrate Melts", Staurt Smedley, Chris Hall and Ernest Yeager, J. Phys. Chem. 76, 1506-7 (1972).
- 47. "Brillouin Scattering in Aqueous Electrolyte Solutions", Arthur Maret and Ernest Yeager, J. Chem. Phys. <u>57</u>, 2225-2227 (1972).

- "Origin of the Low Frequency Sound Absorption in Seawater", E. Yeager, F.H. Fisher, J. Miceli, and R. Bressel, J. Acoust. Soc. Am. <u>53</u>, 1705-1707 (1973).
- 49. "Rayleigh-Brillouin Intensity Ratios in Aqueous Electrolyte Solutions", A. Maret and E. Yeager, J. Chem. Phys. <u>59</u>, 206-212 (1973).
- 50. "Brillouin Scattering in Aqueous Electrolyte Solutions," A. Maret and E. Yeager, J. Acoust. S-c. Am. <u>54</u>, 668-75 (1973).
- 51. "Ultrasonic Velocity Measurements: The Compressibilities of Solutions and Molten Salts", Chris Hall and Ernest Yeager, Techniques of Electrochemistry, E. Yeager and A. Salkind, eds., J. Wiley and Sons-Interscience, New York, Vol. II, Chapter 7, 1973, pp. 399-422.
- 52. Comments on "Hypersonic Velocities in Aqueous Alkali Chloride Solutions", R. Maret and E. Yeager, J. Chem. Phys. 60, 4100-4101 (1974).
- 53. Comment on the paper "Ionic Solvation Numbers from Compressibilities and Ionic Vibraton Potential Measurements", by E. Yeager and R. Zana, J. Phys. Chem. 79, 1228-1230 (1975).
- 54. "Ultrasonic and Hypersonic Properties of Ionic Hydrate Melts", by R. Carpio, F. Borsay, C. Petrovic and E. Yeager, J. Chem. Phys. 65, 29-38 (1976).
- 55. "An Acousto-Electrochemical Effect", by Frank Borsay and Earnest Yeager, Transactions of the Society for Advancement of Electrochemical Science and Technology (SAEST), <u>12</u>, 179-185 (1977).
- 56. "Generation of Ultrasound, at Metal-Electrolyte Interfaces", by F. Borsay and E. Yeager, J. Acoust. Soc. Am. <u>59</u>, 596-598 (1978).
- 57. "Ultrasonic Vibration Potentials", R. Zana and E. Yeager, Modern Aspects of Electrochemistry, Vol. 13, B. Conway and J. Bockris, eds., Plenum Press, New York, 1979.
- 58. "Depolarized Rayleigh Light Scattering Studies of Concentrated Aqueous Nitrate Solutions", R.A. Carpio, M. Mehicic and E. Yeager, J. Chem. Phys. <u>74</u>, 2778 (1981).

APPENDIX B

F

1.	E. Yeager and F. Hovorka, "The Effect of Acoustical Waves on the Hydrogen Electrode", Technical Report No. 1, April (1949), Office of Naval Research Task NR 051-162.
2.	F. Hovorka, E. Yeager, J. Bugosh, H. Chessin and D. Stoicopoulos, "Appparatus for Acoustical Measurements with Pulse-Modulated Ultrasonic Waves", Technical Report No. 2, October (1949), Office of Naval Research, Task NR051-162.
3.	E. Yeager and F. Hovorka, "The Effect of Acoustical Radiations on the Hydrogen Electrode", Technical Report No. 3, April 1950, Office of Naval Research, Task NR-051-162.
4.	D. Stoicopoulos, E. Yeager and F. Hovorka, "Electronic Instrumentation for Overvoltage Measurements", Technical Report No. 4, April (1950), Office of Naval Research, Task NR051-162.
5.	E. Yeager, H. Dietrich, J. Bugosh and F. Hovorka, "An Electrokinetic Probe for the Detection of Ultrasonic Waves", Technical Report No. 5, Feb. (1961), Office of Naval Research, Task NR 051-162.
6.	E. Yeager, T.S. Oey, D. Stoicopoulos, and F. Hovorka, "Electronic Instrumen- tation for Polarization Measurements: An Improved Commutator", Technical Report No. 6, April (1951), Office of Naval Research, Task NR 051-162.
7.	E. Yeager, H. Dietrick and F. Hovorka, "Colloidal Vibration Potentials", Technical Report No. 7 April (1952), Office of Naval Research, Task NR 051-162.
8.	H.J. Dietrick, E. Yeager, J. Bugosh and F. Hovorka, "The Production of Alternative Components in the Potential of a Polarized Hydrogen Electrode with Ultrasonic Waves", Technical Report No. 8, May (1952), Office of Naval Research, Task NR 051-162.
9.	T.S. Oey, E. Yeager and F. Hovorka, "Hydrogen Overvoltage Measurement on Platinum: Part I, The Effect of Ultrasonic Waves on Hydrogen Overvoltage, Part II, Comments on the Kinetics Associated with Hydrogen Overvoltage on a Platinum Surface", Technical Report No. 9 (1952), Office of Naval Research Task NR 051-162.
10.	W. Wolfe, H. Chessin, E. Yeager and F. Hovorka, "The Effects of Ultrasonics on the Electrodeposition of Copper", Technical Report No. 10 (1952), Office of Naval Research, Task NR 051-162.
11.	E. Yeager and F. Hovorka, "A Survey of Electrochemical Applications of Ultrasonic Waves", Technical Report No. 11, November (1952), Office of Naval Research, Task NR 051-162.
12.	E. Yeager, H. Dietrick, J. Bugosh and F. Hovorka, "Ultrasonic Waves and Electrochemistry: Part I, A Survey of the Electrochemical Applications of Ultrasonic Waves, Part II: Colloidal and Ionic Vibration Potentials, Part III: An Electrokinetic Effect Produced by Ultrasonic Waves, Part IV: The Production of Alternative Compounds in the Potential of a Polarized Hydrogen Electrode with Ultrasonic Waves" Technical Report No. 12 (1952), Office of Naval Research, Task NR 051-162.

A State of the sta

- F. Saunders, E. Yeager and F. Hovorka, "The Frequency Characteristics of Acousto-Electrochemical Effects" The Electrokinetic and Polarized Gas Electrode Effects", Technical Report No. 13, September (1953), Office of Naval Research, Task NR 384-305.
- W. Wolfe, H. Chessin, E. Yeager and F. Hovorka, "The Effect of Ultrasonic Waves on the Electrodeposition of Copper", Technical Report No. 14, December (1954) Office of Naval Research, Task NR 051-162.
- R. Penn, E. Yeager and F. Hovorka, "The Effect of Ultrasonic Waves on the Electrodeposition of Nickel", Technical Report No. 15, April (1955), Office of Naval Research, Task NR 384-305.
- R. Penn. E. Yeager and F. Hovorka, "The Interaction of Ultrasonic Waves with Concentration Gradients", Technical Report, No. 16, February (1955), Office of Naval Research, Task NR 384-305.
- M. Del Duca, E. Yeager, M.O. Davies and F. Hovorka, "Isotopic Techniques in the Study of the Sonochemical Formation of Hydrogen Peroxide", Technical Report No. 17, December (1956), Office of Naval Research, Task NR 384-305.
- W. Roberts, E. Yeager and F. Hovorka, "The Ultrasonic Degradation of Polymers", Technical Report No. 18, January (1957), Office of Naval Research, Task NR 384-305.
- E. Yeager, J. Booker and F. Hovorka, "Quantitative Measurements of Ionic Vibration Potentials", Technical Report No. 19, August (1957), Office of Naval Research, Task NR 384-305.
- J. Dereska, E. Yeager and F. Hovorka, "Quantitative Measurements of Colloidal Vibration Potentials", Technical Report No. 20, December (1958), Office of Naval Research, Task NR 384-305.
- I. Galperin, E. Yeager and F. Hovorka, "A.C. Streaming Potentials", Technical Report No. 21, December (1958), Office of Naval Research, Task NR 384-305.
- 22. E. Yeager, "Acousto-Electrochemical Effects in Electrode Systems", Technical Report No. 22, May (1959), Office of Naval Research, Task NR 384-305.
- J. Dereska, E. Yeager and F. Hovorka, "Colloidal Vibration Potentials in Silica Suspensions", Technical Report No. 23, December (1960), Office of Naval Research, Task NR 384-305.
- 24. E. Yeager, "Fundamentals and Processing Applications for Sound Waves in Chemistry", Technical Report No. 24, July (1961), Office of Naval Research, Task NR 384-305.
- J. Stuehr and E. Yeager, "Ultrasonic Relaxation in Electrolyte Solution: I. A Review", Technical Report No. 25, July (1962), Office of Naval Research, Task NR 384-305.
- 26. J. Stuehr, E. Yeager, T. Sachs and F. Hovorka, "Ultrasonic Relaxation in Electrolytic Solutions Part II; The Hydrolysis of Potassium Cyanide", Technical Report No. 26, September (1962), Office of Haval Research, Task NR 384-305.

- 27. H. Hoffmann, J. Stuehr and E. Yeager, "Studies of Relaxation Effects in Electrolytic Solutions with the Pressure-Step Method", Technical Report No. 27, June (1964), Office of Naval Research, Task NR 384-305.
- 28. E. Yeager, "Ultrasonic Studies of Electrolytes", Technical Report No. 28, August (1965), Office of Naval Research, Task NR 384-305.
- 29. R. Zana and E. Yeager, "Ultrasonic Vibration Potentials and Their Use in the Determination of Ionic Partial Molal Volumes", Technical Report No. 29, June (1966), Office of Naval Research, Task NR 384-305.
- R. Zana and E. Yeager, "Quantitative Studies of Ultrasonic Vibration Potentials in Polyelectrolyte Solutions", Technical Report No. 30, Feburary (1967), Office of Naval Research, Task NR 384-305.
- 31. R. Zana and E. Yeager, "Ultrasonic Vibration Potentials in Tetraalkylammonium Halide Solutions", Technical Report No. 31, February (1967), Office of Naval REsearch, Task NR 384-305.
- 32. L. Goldfard and E. Yeager, "Ultrasonic Studies of Diffusion Controlled Ionic Association-Dissociation", Technical Report No. 32, January (1968), Office of Naval Research, Task NR 384-305.
- H. Hoffmann and E. Yeager, "Pressure Shock Technique for the Study of Chemical Relaxation", Technical Report No. 33, March (1968), Office of Naval Research, Task NR 384-305.
- 34. R. Zana and E. Yeager, "Ultrasonic Vibration Potentials and Micelle Formation", Technical Report No. 34, September (1968), Office of Naval Research, Task Nr 384-305.
- LeRoy G. Jackopin and E. Yeager, "Ultrasonic Absorption in Electrolytic Solutions", Technical Report No. 35, June (1969), Office of Naval Research, Task NR 384-305.
- 36. H. Hoffman and E. Yeager, "The Effect of Various Inner Coordination Sphere Ligands on the Dissociation Rate of Nickel Malonate Complexes", Technical Report No. 36, March (1970), Office of Naval Research, Task NR 384-305.
- 37. LeRoy G. Jackopin and E. Yeager, "Ultrasonic Relaxation in Manganese Sulfate Solutions", Technical Report No. 37, March (1970), Office of Naval Research, Task NR 384-305.
- LeRoy G. Jackopin and E. Yeager, "Ultrasonic Relaxation in Aqueous Acetic Acid Solutions", Technical Report No. 38, February (1981), Office of Naval Research Task NR 384-305.
- 39. C. Hall and E. Yeager, "A Review of Ultrasonic Measurements in Ionic Solutions and Molten Salts", Technical Report No. 39, July (1972), Office of Naval Research, Task NR 384-305.
- 40. A.R. Maret and E. Yeager, "Brillouin Scattering in Aqueous Electrolyte Solutions", Technical Report No. 35, June (1969), Office of Naval Research, Task NR 384-305.

- 41. A.R. Maret and E. Yeager, "Rayleigh-Brillouin Intensity Ratios in Aqueous Electrolyte Solutions", Technical Report No. 41, November (1972), Office of Naval Research, Task NR 384-305.
- 42. E. Yeager, F.H. Fisher, J. Miceli and R. Bressel, "Origin of the Low Frequency Sound Absorption in Sea Water", Technical Report No. 42, January (1973), Office of Naval Research, Task NR 384-305.
- 43. R. Corpio, F. Borsay, C. Petrovic and E. Y eager, "Ultrasonic and Hypersonic Properties of Ionic Hydrated Melts", Technical Report No. 43, July (1975), Office of Naval Research, Task NR 384-305.
- 44. F. Borsay and E. Yeager, "Generation of Ultrasound at Metal Electrolyte Interfaces", Technical Report No. 44, August (1977), Office of Naval Research, Task NR 384-305.
- 45. R. Zana and E. Yeager, "Ultrasonic Vibration Potentials", Technical Report No. 45, November (1978), Office of Naval Research, Task NR 384-305.
- 46. M.A. Barrett-Bültepe, M.E. Gültepe and E.B. Yeager, "Acoustic Studies of Colloidal Suspensions and Marine Sediments. Part I. Theoretical Considerations and High Frequency Measurements", Technical Report No. 46, January (1980), Office of Naval Research, Task NR 384-305.
- R. Corpio, M. Mehicic and E. Yeager, "Depolarized Rayleigh Light Scattering Studies of Concentrated Aqueous Nitrate Solutions", Technical Report No. 47, December 15 (1981), Office of Naval Research, Task NR 384-305.
- 48. M.A. Barrett-Gültepe, M.E. Gültepe and E.B. Yeager, "Computer Controlled Resonator Measurements with a 12-Liter Pyrex Sphere and a 100-Liter Titanium Sphere", Technical Report No. 48, June 1981, Office of Naval Research, Task NR. 384-305.

	omplishment	Significance	Uoworkers	
	The first detection and quantitative studies of ionic vibration potentials	Yields absolute partial molal volumes and important information concerning ion-solvent interaction in electrolytes.	R. Zana R. Dietrick	
5.	The first detection and quantitative measurements of polyelectrolyte vibration potentials; the development of a theoretical treatment of poly- electrolyte vibration potentials.	Information on counter ion binding and polyelectro- lyte configuration in systems of both biological and industrial interest.	R. Zana J. Booker	·
ň	The application of the ionic vibration potential technique to the study of micelles and the obtaining of evidence for the formation of clusters prior to micelle formation.	Results of interest from the standpoint of biological systems and detergent physical chemistry.	R. Zana	-24
	The quantitative study of colloidal vibration potentials.*	Quantitative verification of theory of charge distribution about colloidal particles in electro- lytic solutions - of both biological and industrial interest.	J. Dereska J. Booker M. E. Gültepe Y. Chonde	
ŝ	Ultrasonic absorption measurements in colloidal dispersions in electrolytic solutions and identification of various loss mechanisms. ⁺	Dispersed material in seawater contributes to sound absorption and scattering in long range sound transmission in the sea.	L. Jackopin F. Borsay M. E. Gultepe	
	Correction of erroneous data in the literature for ultrasonic relaxation in 2-2 electrolytes; development of a two-step rather than three-step model; quantitative studies of second order diffusion controlled processes in such electrolytes.	Understanding of fast chemical processes in electrolytic solutions; the principal process (MgSO4) responsible for ultrasonic absorption in seawater below 10 ⁵ Hz.	L. Jackopin, L. Godlfarb, J. Stuehr	

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+ Research in progress during the past year.

	Identification of various ultrasonic relaxation effects in other electrolytes including the tetraalkyl annonium salts, and weak electrolyte and salts thereof,	Understanding of the dynamics of electrolytic solutions; of interest to physical chemist and biologist.	L. Jackopín, J. Broadhead	
•	tation of these relaxations. Quantitative results for the helix-random coil transformation in the model amino acid compound, poly-L-glutamic acid, and the finding that the transition is far	Helpful information to molecular biologists in understanding the properties of amino acids.	J. Stuehr, A. Berksdele	
÷	Development of shock wave technique in a practical form for the study of relaxa- tion processes in electrolytes at times as short as 10 ⁻⁶ sec; use of this tech- as short as 10 ⁻⁶ sec; use of this tech- nique to obtain the first observation of relaxation in magnesium sulfate solutions,	Method can be used to study relaxation at frequencies too low for practical ultrasonic laboratory measurements; has confirmed MgSO _h relaxation (the sea vater problem).	R. Hoffmann	-2
o	Identification of a relaxation in the borate-boric acid system in sea water with relaxation times of ~160 µ sec using temperature-jump and shock wave techniques.	Provides the explanation for the low frequency relaxation encountered in acoustic propaga- tion in sea water.	R. Bressel, J. Micelli, F. Fisher	5-
ंत	Brillouin and Rayleigh scattering mea- surements in electrolytic solutions; measurements of hypersonic velocities and absorption; measurements of inten- sity ratios of Rayleigh to Brillouin	Extends ultrasonic measurements to gigahertz frequencies; confirmation of theory of con- centration fluctuations in electrolytic solutions.	A. Maret	
2	Components. Brillouin and Rayleigh (polarized and depolarized: scattering studies in hyd- rate melts (including supercooled) and molten salts; further evidence for visco- elastic relaxation in these systems. ⁺	Information on liquid dynamics; helpful in understanding the super-cooling phenomenon.	R. Carpio C. Petrovic F. Borsay B. Simic-Gli	&vas)

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Research in progress during the past year.

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Api	pendix C (continued)		ı I	•
ŗ	LOW angle Brillouin scattering studies in electrolytes at frequencies down to low megahertz.	Comparison of temporal and spatial relaxation; helpful in understand- ing phonon properties of liquids.	F. Borsay	
.41	Ultrasonic absorption-velocity relaxation studies in hydrate melts (including supercooled). Identi- fication of relaxation effects. ⁺	Helpful in understanding liquid dynamics and supercooling phenomena; interesting system for comparison of chemical relaxa- tion and visco-elastic theory.	F. Horsey, R. Bressel, S. Smedley, C. Hall	
15.	The discovery of the acousto-electro- kinetic effect.	Has been used as probe for examination of acoustical fields.	H. Dietrick, F. Saunders	
16.	Quantitative studies of the effects of sound waves (with and without cavitation) on mass transfer and boundary layers using schlieren techniques.	Demonstrated that ultrasonically produced cavitation greatly increases mass and heat transfer at solid-liquid boundaries.	R. Penn	
11.	Isotopic equilibration studies of cavitation, which have helped to define the temperature limits real- ized within cavitation bubbles during compression or collapse.	Provides explanation for chemical effects produced by intense sound waves.	M. Del Duca	_
18.	The establishment of the mechanism for the effects of intense sound waves on electrodeposition, corro- sion and other electrode processes.	Potential application of intense sound vaves to improve electroplating.	R. Penn, W. Wolfe	-
19.	Elucidation of the mechanism for ultrasonic degradation of polymers and also the initiation and promotion of polymerization.	Provides bases for understanding damage to biological systems caused by intense sound waves.	W. Roberts, R. Fox	
20.	Elucidation of mechanism for ultra- sonic emulsification; role of surface waves.	Considerable promise as method for producing emulsions.	A. Patale	
21.	Interface electromodulation acoustic effect. ⁴	Information concerning the structure of water at electrode-electrolyte interface.	F. Borsey M. E. Gulte	
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22.	The first detection and qualitative study	Provides in
	of the effect of hetero-deflocculation of	of sound pro
	two disimilar mineral grains on the velocity	component co
	of sound in concentrated dispersions of	
	kaoline-montmorillonite mixtures. ⁺	

- 23. A micro-computer controlled velocity and absorption measurements with cylindrical and spherical resonators and using this system with a 100 L titanium spherical resonator.⁺
- 24. The first detection and qualitative study of the effect of adsorbed species and configurational changes of this adsorbed layer on the velocity of sound in the concentrated dispersions of a model colloid.⁺
- 25. Development of computerized resonator system for absorption measurements in electrolytes and colloidal systems

M.E. Gültepe M.A. Barrett-M.A. Barrett-M.A. Barrett-M.E. Gültepe M.E. Gültepe Gültepe Gültepe Gültepe The computer controlled experiments gives better opagation in sediments and the multidefined relaxation curves with greater accuracy Understanding of the structure of the adsorbed macromolecules at electrochemical interfaces. cormation for better understanding olloidal dispersions. and reproducibility.

Very substantially extends the capability of M.E. Gultepe M.A. Barrettthe resonator method. Gultepe

+Research in progress during the past year.

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