

Variations in the Ultrasonic Velocity within Electrolytic Solutions under Ionic Drift

S. B. Agarwal^A and *V. P. Bhatnagar*^B

^A Mahanand Mission Harijan College, Ghaziabad, India.

^B Physics Department, Delhi College of Engineering, Delhi-110006, India.

Abstract

Measurements are presented which show that the ultrasonic velocity v in aqueous solutions of common electrolytes increases with the ionic drift current density j , such that $\Delta v \propto \exp(j^{\frac{1}{2}})$.

Introduction

It is well known that, when an ultrasonic wave propagates in an electrolytic solution, interaction between the mobile charge carriers gives rise to an electroacoustic effect (Debye 1933; Yeager *et al.* 1949, 1951, 1953; Derouet and Denizot 1951) and the electrical conductivity of the medium changes (Fox *et al.* 1946; Altenburg and Dorr 1952; Agarwal and Bhatnagar 1975, 1976). Although many experimental studies have been made on the velocity and attenuation of ultrasonic waves in electrolytic solutions, no attempts have yet been made to relate these propagational characteristics to the underlying inter-ionic interactions. Explicit experimental results along these lines may be of some importance to underwater signalling and communication technology, as well as being of theoretical interest.

Several attempts have been made to control the attenuation of ultrasonic waves by applying external electric fields and to develop travelling wave amplifiers for ultrasonic waves, but these have been mainly confined to propagation in semiconducting and piezoelectric materials (Hutson 1961; Smith 1962; Wang 1962; McFee 1963, 1966). Apart from the early work of Nolle (1948) and Krishnamurthy (1951), no serious investigations have been made of electrolytic solutions under charge-drift conditions. Nolle (1948) investigated a variety of liquids (polar, nonpolar, conducting and nonconducting) and concluded that an external electric field did not alter the velocity of propagation of an ultrasonic wave in a conducting liquid. He attributed all measureable changes in velocity to the effects of ohmic heating, caused by the passage of the AC current through the conducting liquid. Krishnamurthy (1951), in a study of several electrolytic solutions by an optical diffraction method, reported marked increases in the ultrasonic velocity, but he did not publish the magnitudes of the current and voltage employed so that no quantitative relation can now be obtained from his results.

Clearly this important subject requires more detailed investigation, and so the present authors have undertaken a quantitative study of the velocity of ultrasonic propagation in several electrolytic solutions under the influence of the ionic drift obtained from the passage of a 50 Hz AC current. The ultrasonic velocity data were

Table 1. Variation of ultrasonic velocity in ionic solutions with drift current density
 The ultrasonic velocities v_x and adiabatic compressibilities β_x are for ionic drift current densities i_x (kA m^{-2}), where $i_x = 0.83x$ for $x = 0, 1, \dots, 4$

Conc. (M)	ρ (g cm^{-3})	T ($^{\circ}\text{C}$)	v_0 (m s^{-1})	v_1 (m s^{-1})	v_2 (m s^{-1})	v_3 (m s^{-1})	v_4 (m s^{-1})	β_0 (TPa^{-1})	β_1 (TPa^{-1})	β_2 (TPa^{-1})	β_3 (TPa^{-1})	β_4 (TPa^{-1})
(a) Sodium acetate												
3.0	1.1095	30	1760	1766	1776	1790	1810	2.913	2.893	2.859	2.813	2.752
2.0	1.0720	30	1671	1675	1682	1690	1700	3.341	3.321	3.298	3.266	3.228
1.0	1.0355	30	1586	1588	1593	1599	1606	3.840	3.832	3.808	3.779	3.747
0.5	1.0159	30	1547	1548	1551	1555	1560	4.113	4.110	4.089	4.074	4.048
(b) Calcium acetate												
1.0	1.0700	35	1601	1606	1616	1630	1652	3.619	3.597	3.553	3.491	3.399
(c) Lead acetate												
1.0	1.2240	35	1452	1456	1462	1472	1490	3.875	3.855	3.821	3.770	3.681
(d) Zinc sulphate												
1.0	1.1510	35	1607	1617	1632	1654	1688	3.366	3.323	3.260	3.177	3.049
(e) Sodium chloride												
0.0193	1.1917	30	1801	1806	1816	1830	1850	2.589	2.574	2.544	2.507	2.453
(f) Sodium iodide												
0.0894	1.4980	30	1525	1528	1535	1550	1576	2.872	2.860	2.833	2.779	2.687
(g) Potassium chloride												
0.0569	1.1285	30	1649	1652	1658	1668	1681	3.260	3.248	3.225	3.186	3.137
(h) Potassium iodide												
0.0444	1.2658	30	1484	1490	1499	1515	1544	3.588	3.560	3.518	3.444	3.153

obtained by an interferometric technique. Data on attenuation, obtained by a pulse technique, are still being examined; it is hoped that they will be published in the near future.

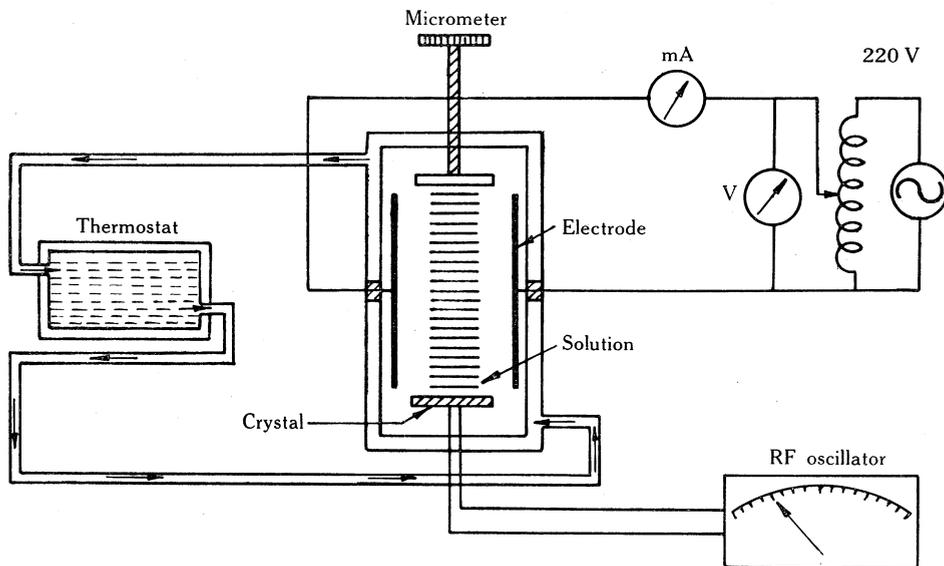


Fig. 1. Schematic diagram of the interferometer cell arrangement used to demonstrate the dependence of the ultrasonic velocity on the ionic drift current.

Experimental Arrangement

The experimental arrangement is shown schematically in Fig. 1. The well-known interferometric technique (Pierce 1925; Greenspan 1950; Hall and Yeager 1973) was used. The cell containing the electrolytic solution has a capacity of 35 cm^3 and the two thin electrodes have dimensions of $2 \times 3 \text{ cm}^2$. The interior of the cell could be maintained at a constant thermostatically controlled ($\pm 0.1^\circ\text{C}$) temperature between room temperature and 80°C by the circulation of water within a surrounding outer jacket.

For the present experiment to succeed, it was essential to pass current through the solution for as short a period as possible to minimize the effects of ohmic heating. Strictly speaking, a DC current should have been used but this leads to deposition at the electrodes, which completely disturbs the state of the solution. The ionic drift motion was thus provided by a low frequency (50 Hz) AC current. This produces a 10 ms period of drift reversal, which is many orders of magnitude greater than the ionic relaxation time ($\sim 1 \mu\text{s}$). The AC current was allowed to flow for 30 s. We assume (but were unable to demonstrate with our apparatus) that any changes in the ultrasonic velocity due to ionic drift should have reached a steady value within 30 s. However, even with an AC source, a feeble deposition occurred at the electrodes after prolonged use. Care was taken to present clear electrodes and clean electrolytes during the experiments.

We calibrated the apparatus in terms of the standard available data prior to each run. The velocity of ultrasonic propagation was then determined by interferometry for the following solutions of electrolytes: sodium acetate, calcium acetate, lead

acetate, zinc sulphate, sodium chloride, sodium iodide, potassium chloride and potassium iodide. The velocities were measured for ionic drift current densities of $0, \sigma, 2\sigma, 3\sigma$ and 4σ , where $\sigma = 0.83 \text{ kA m}^{-2}$. Corresponding values for the adiabatic compressibility β were then calculated from the relation

$$\beta = 1/v^2\rho,$$

where v is the ultrasonic velocity and ρ is the density of the solution. For sodium acetate, the velocity measurements were taken over a range of concentrations from $0.5\text{--}3.0 \text{ M}$. The data for calcium acetate, lead acetate and zinc sulphate are for 35°C ; the rest are for 30°C .

Results and Discussion

The experimental results are shown in Table 1, in which the velocities v_α and compressibilities β_α correspond to current densities of $0.83\alpha \text{ kA m}^{-2}$, with $\alpha = 0, 1, \dots, 4$. It is clear from these results that v_α increases markedly with increasing α (i.e. with increasing ionic current density). A semilogarithmic plot of $\log_{10}(v_\alpha - v_0)$ versus $\alpha^{\frac{1}{2}}$ gives a set of parallel straight lines for these data. We thus have the following relation for the dependence of the change in velocity Δv on the current density j

$$\Delta v = a \exp(bj^{\frac{1}{2}}) \quad \text{for} \quad j \gtrsim 1 \text{ kA m}^{-2},$$

with perhaps

$$\Delta v = a\{\exp(bj^{\frac{1}{2}}) - 1\} \quad \text{for} \quad j \lesssim 1 \text{ kA m}^{-2},$$

where a and b are constants.

Nolle's (1948) attribution of this effect to ohmic heating does not seem likely in our case because of the above relations. Ohmic heating effects should be proportional to j^2 and should be many orders of magnitude less than the phenomenon we have observed. We therefore conclude that we have discovered a genuine dependence of the ultrasonic velocity on the ionic current density. We have been unable so far to explain our results in terms of a model of coupling between the ultrasonic waves and the drift velocity of the ions. Perhaps further experimental investigations may elucidate new information regarding interionic collisions.

Acknowledgments

One of us (S.B.A.) wishes to thank the University Grants Commission, New Delhi, for the award of a research grant. We also thank Dr V. N. Bindal, Head of the Ultrasonic Instrumentation Division, National Physical Laboratory, New Delhi, for suggesting improvements in the design of the interferometer cell, and a referee for pointing out the form of the empirical relationship presented above.

References

- Agarwal, S. B., and Bhatnagar, V. P. (1975). *Indian J. Pure Appl. Phys.* **13**, 738.
- Agarwal, S. B., and Bhatnagar, V. P. (1976). *Jpn J. Appl. Phys.* **15**, 2337.
- Altenburg, K., and Dorr, G. Z. (1952). *Phys. Chem.* **200**, 158.
- Debye, P. (1933). *J. Chem. Phys.* **1**, 13.
- Derouet, B., and Denizot, F. (1951). *C. R. Hebd. Seanc. Acad. Sci. Paris* **233**, 368.
- Fox, F. E., Herzfeld, K. P., and Rock, C. D. (1946). *Phys. Rev.* **70**, 329.
- Greenspan, M. (1950). *J. Acoust. Soc. Am.* **22**, 568.

- Hall, C., and Yeager, E. (1973). In 'Techniques of Electrochemistry', Vol. 2 (Eds E. Yeager and A. L. Salkind) p. 407 (Wiley: New York).
- Hutson, A. R. (1961). *J. Appl. Phys.* **32**, 2287.
- Krishnamurthy, B. H. (1951). *J. Sci. Ind. Res. (New Delhi)* B **10**, 149.
- McFee, J. H. (1963). *J. Appl. Phys.* **34**, 1548.
- McFee, J. H. (1966). In 'Physical Acoustics', Part IVA (Ed. W. P. Mason), p. 1 (Academic: New York).
- Nolle, A. W. (1948). *J. Appl. Phys.* **20**, 589.
- Pierce, G. W. (1925). *Proc. Am. Acad. Arts Sci.* **60**, 271.
- Smith, R. W. (1962). *Phys. Rev. Lett.* **9**, 87.
- Wang, W. C. (1962). *Phys. Rev. Lett.* **9**, 443.
- Yeager, E., Bugosh, J., and Hovorka, R. (1951). *Proc. Phys. Soc. London* B **64**, 83.
- Yeager, E., Bugosh, J., Hovorka, R., and McCarthy, J. (1949). *J. Chem. Phys.* **17**, 411.
- Yeager, E., Dietrick, H., and Hovorka, F. (1953). *J. Acoust. Soc. Am.* **25**, 456.

Manuscript received 28 September 1977, revised 19 May 1978

