1164. *Ultrasonic Studies of Electrolyte Solutions. Part I. Ultrasonic Velocities in Solutions of Inorganic Salts.*

By D. S. ALLAM and W. H. LEE.

Two types of ultrasonic interferometer have been constructed and used to measure the wavelengths of ultrasonic standing waves in solutions of inorganic salts in water, methanol, and ethanol, and also in the pure solvents. Ultrasonic velocities have been calculated from these measurements.

THERE have been several previous studies of the passage of ultrasonic (compressional) waves through aqueous electrolyte solutions;[1,2] however, no systematic investigation, comparing the results for a range of solutes in different solvents, has been reported. As part of a study of the solvation and structure-changing effects of ions in polar solvents, we have measured the velocities of ultrasonic waves in the following solutions:

LiCl a,m	NaCl a,m	KCl a	NH_4Cl a,m	$MgCl_2$ a	$AgNO_3$ a
LiBr a,m,e	NaBr a,m,e	KBr a,m	NH_4Br a,m,e	$MgSO_4$ a	
LiI a,m,e	NaI a,m,e	KI a,m	NH_4I a,m,e		
$LiNO_3$ a,m,e	$NaNO_3$ a,m	KNO_3 a	NH_4NO_3 a,m,e		

a, aqueous solution; m, methanol solution; e, ethanol solution.

EXPERIMENTAL

Apparatus.—Two different types of ultrasonic interferometer have been constructed, and are now briefly described; further details of their construction are given elsewhere.[3]

The first type, shown in Fig. 1, is generally similar to that described by Hubbard and Loomis.[4]
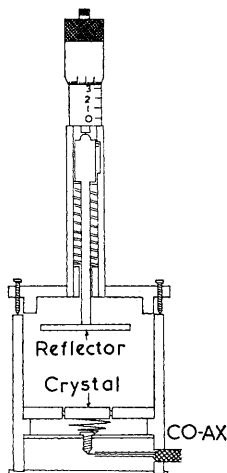

FIG. 1. Hubbard and Loomis interferometer.

The body of the instrument is of brass; a cylindrical X-cut quartz crystal, of diameter 3 cm., and of resonant frequency (after mounting) 263·9 kc./sec., is supported horizontally in the base by four thin rubber pads. The solution under investigation is contained in a polythene cup, resting on the upper crystal face. A flat brass plate, adjusted to be accurately parallel to the upper surface of the crystal, can be raised or lowered through the solution by means of a precision micrometer, the vertical displacement being measurable to 0·01 mm.

The crystal is driven, *via* a power amplifier, by means of a Colpitt's oscillator of carefully-

[1] A. G. Passynski, *Acta Physicochim. U.R.S.S.*, 1938, **8**, 385.
[2] S. Barnartt, *Quart. Rev.*, 1953, **7**, 84.
[3] D. S. Allam, Ph.D.Thesis, London 1963.
[4] J. C. Hubbard, and A. L. Loomis, *Phil. Mag.*, 1928, **5**, 1177.

matched frequency (this frequency is maintained constant by means of a second crystal). Connexions are made to the gold-sputtered lower face of the crystal by means of screened 75-ohm coaxial cable, and (*via* the cable screening) to the brass body; no second connexion to the crystal is necessary because of the capacitative coupling to the upper face.

The passage of the reflector through nodal positions sets up standing waves in the solution, and causes the loading of the crystal to change; small variations in voltage across the crystal are detected by a sensitive valve voltmeter. If the micrometer reading at the first node is A, and that at the nth node is B, the half-wavelength is given by:

$$\lambda/2 = (B - A)/(n - 1) \qquad (1)$$

In use, the interferometer was maintained at $25\cdot00° \pm 0\cdot01°$.

The second type of interferometer (Fig. 2) was designed to improve the accuracy of half-
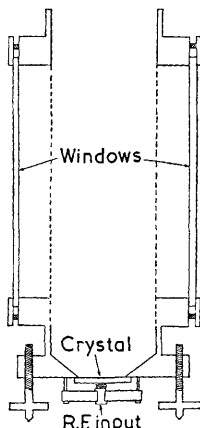

FIG. 2.   Debye and Sears interferometer.

wavelength measurement, and makes use of the technique described by Debye and Sears.[5] In this instrument, standing waves in the solution caused periodic density variations, and these are made visible by the Schlieren effect. The interferometer body is of stainless steel, with optical-glass windows; the solution is contained in a rectangular optical-glass cell resting on the upper surface of the crystal (of diameter $2\cdot5$ cm., and resonant frequency, after mounting, $973\cdot2$ kc./sec.). The method of driving this crystal is similar to that already described.

In this instrument the reflector is the upper surface of the solution, which may be raised or lowered by insertion of a glass rod. The half-wavelength is measured by illuminating the solution with a collimated beam of light and counting the number of nodes within a known distance by means of a cathetometer. The instrument was maintained at $25\cdot0° \pm 0\cdot1°$ inside a thermostat-controlled enclosure.

The second type of interferometer is rather easier to set up, since the liquid surface may easily be made parallel to the upper crystal face. Further, variations in mains-supply voltage merely produce small changes in intensity of the Schlieren bands; in the first instrument, such variations may give rise to spurious changes in valve voltmeter reading.

RESULTS

For all types of wave motion, the velocity of propagation, v, the frequency, ν, and the wavelength, λ, are related:

$$v = \nu\lambda \qquad (2)$$

Hence, from the frequency of the generating crystal and the measured half-wavelength, the velocity in a given medium can be calculated.

Ultrasonic velocities in the pure solvents at 25° are recorded in Table 1; the frequency identifies the interferometer used for a particular series of measurements.

There is probably a small but significant difference between velocities measured at the two frequencies, and accordingly the measurements on solutions were made with the second instrument,

[5] P. Debye and F. W. Sears, *Proc. Nat. Acad. Sci. U.S.A.*, 1932, **18**, 409.

TABLE 1.

Frequency (kc./sec.)	Velocity (m./sec.)		
	Water	Methanol	Ethanol
263·9	1498·8 ± 0·6*	1104·1 ± 0·7	1144·7 ± 0·7
973·2	1497·9 ± 0·6	1101·7 ± 0·7	1143·1 ± 0·7

* Standard deviation of 12 results.

of frequency 973·2 kc./sec. The reproducibility of results is slightly better in water than in the alcohols, probably due to the difficulty of preparing and maintaining absolutely anhydrous solvents. The results are in good agreement with those of other recent investigations, *e.g.*, water, 1496·7 (Owen and Simons[6]), 1498·1 (Hubbard and Loomis[4]), 1497·1 (Owen and Kronick[7]); methanol, 1100 (Rao and Rao[8]), 1102·4 (Golik *et al.*[9]); ethanol, 1140 (ref. 8.), 1141·6 (ref. 9).

Detailed results of ultrasonic velocity measurements of the solutions are given elsewhere,[3] but typical results are summarised in Figs. 3, 4, and 5.
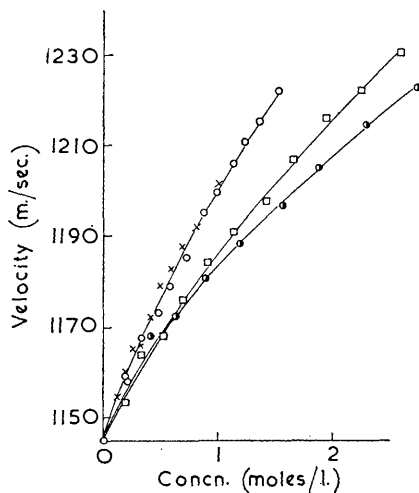

FIG. 3. Variation of velocity with concentration for some salts in ethanol.
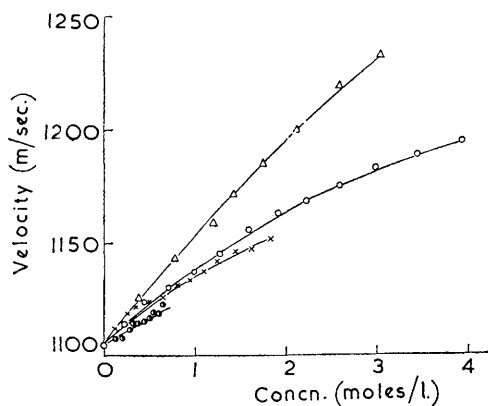
×, LiNO$_3$.   O, LiCl.   □, LiBr.   ◖, LiI.

FIG. 4. Variation of velocity with concentration for some salts in methanol.

△, LiI.   O, NaI.   ×, NH$_4$I.   ◖, KI.

DISCUSSION

The majority of solutions show an increase in the ultrasonic velocity with increasing solute concentration; however, aqueous solutions of lithium, sodium, potassium, and

[6] B. B. Owen and H. L. Simons, *J. Phys. Chem.*, 1957, **61**, 479.
[7] B. B. Owen and P. L. Kronick, *J. Phys. Chem.*, 1961, **65**, 84.
[8] B. R. Rao and K. S. Rao, *Proc. Phys. Soc.*, 1959, **73**, 239.
[9] A. Z. Golik, Yu. I. Shimanskii, and N. M. Kobüchuk, *Ukrain. fiz. Zhur.*, 1958, **3**, 537.

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ammonium iodides, and of silver nitrate, exhibit a maximum, minimum, or point of inflection in the velocity versus solute molarity curve, and show regions of decreasing velocity with increasing solute concentration (Fig. 6). This behaviour has been reported previously[10,11] and ascribed to the presence of heavy ions. We have found that aqueous solutions of nitric and hydrochloric acids behave similarly (Fig. 6), and a more general explanation may be
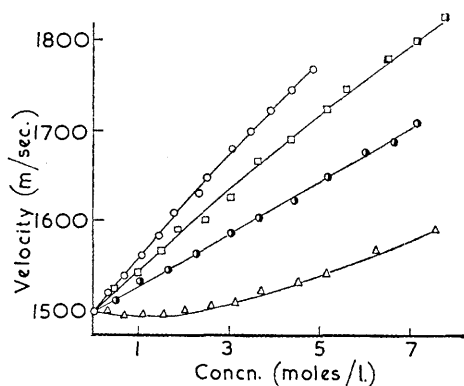
FIG. 5.   Variation of velocity with concentration for some aqueous solutions.

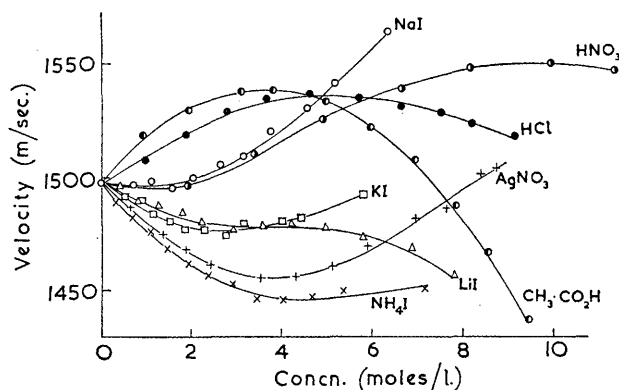○, NaCl.   □, NaNO$_3$.   ◗, NaBr.   △, NaI.

FIG. 6.   Variation of velocity with concentration for some aqueous solutions.

obtained from equation (3), which relates the ultrasonic velocity, v, with the compressibility, β, and the density, ρ, of the solution:

$$v = (\beta\rho)^{-1/2} \qquad (3)$$

The variation in velocity with solute molarity c may then be expressed:

$$dv/dc = -v(1/\rho \cdot d\rho/dc + 1/\beta \cdot d\beta/dc)/2 \qquad (4)$$

It will be shown in a subsequent paper in this series that the compressibility decreases monotonically with increasing molarity, so that the terms $1/\rho \cdot d\rho/dc$ and $1/\beta \cdot d\beta/dc$ are of opposite sign, and their relative magnitudes decides the sign of dv/dc. This is illustrated in Table 2 for the electrolytes hydrochloric acid and silver nitrate, for which the velocity–concentration curves have different signs initially (Fig. 6). Also, if $1/\rho \cdot d\rho/dc + 1/\beta \cdot d\beta/dc = 0$, a turning-point will appear in the velocity–molarity graph.

For most solutions, $-1/\beta \cdot d\beta/dc$ is greater than $1/\rho \cdot d\rho/dc$, so that dv/dc is positive. A negative region of dv/dc may be variously ascribed to a heavy anion (as in the series of iodides), to incomplete dissociation (as in acetic acid solutions), or to ion-pair formation

[10] S. V. Subrahmanyam, *Trans. Faraday Soc.*, 1960, **56**, 971.
[11] M. G. Seshagri Rao and B. R. Rao, *Nature*, 1961, **191**, 164.

TABLE 2.

c	v	ρ	β	$\Delta\rho/\Delta c$	$-\Delta\beta/\Delta c$	$1/\rho . \Delta\rho/\Delta c$	$-1/\beta . \Delta\beta/\Delta c$
			HCl				
0·9242	1507·7	1·0132	43·42				
				0·01716	1·422	0·01418	0·0335
1·864	1519·4	1·0293	42·08				
				0·01638	1·216	0·0158	0·0291
2·781	1528·9	1·0443	40·97				
				0·01618	0·960	0·0153	0·0236
3·646	1534·3	1·0584	40·14				
			AgNO₃				
0·6287	1486·8	1·0851	41·69				
				0·1370	3·950	0·121	0·098
1·347	1474·7	1·1837	38·85				
				0·1382	3·621	0·114	0·0959
1·860	1467·8	1·2549	36·99				
				0·1360	3·290	0·106	0·0919
2·388	1462·0	1·3268	35·26				
				0·1340	2·950	0·0951	0·0835
3·564	1455·7	1·4835	31·81				

c is the solute molarity, *v* the ultrasonic velocity (m./sec.), ρ the density, and β the adiabatic compressibility of the solution.

(*e.g.*, silver nitrate: Robinson and Davies[12] report p$K = -0.2$ for the equilibrium $Ag^+NO_3^- \rightleftharpoons Ag^+ + NO_3^-$). However, magnesium sulphate solutions show positive dv/dc curves, although ion-pair formation is well established in this system (p$K = 2.23$, Davies[13]).

For those aqueous solutions which show a continuous increase in velocity with solute molarity, the velocity decreases along the series $Na^+ > Li^+ > K^+ > NH_4^+$ for all anions, and along the series $Cl^- > NO_3^- > Br^- > I^-$ for all cations. These series become $Li^+ > Na^+ > NH_4^+ > K^+$, and $Cl^- \geqslant NO_3^- > Br^- > I^-$, in both methanol and ethanol solutions, reflecting the changes in the size of the solvated species in these media. In all solutions the ultrasonic velocity decreases with increasing mass of the anion, as pointed out by Barthel;[14] there appears to be no similar correlation with the mass of the cation.

DEPARTMENT OF CHEMISTRY, BATTERSEA COLLEGE OF TECHNOLOGY,
LONDON, S.W.11. *[Received, August 6th, 1964.]*

[12] R. A. Robinson and C. W. Davies, *J.*, 1937, 574.
[13] C. W. Davies, *Trans. Faraday Soc.*, 1927, **23**, 351.
[14] R. Barthel, *J. Acoust. Soc. Amer.*, 1954, **26**, 227.