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The Relation between Ultrasonic Velocity and Viscosity in Aqueous Solutions of Electrolytes

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From the experimental data on the ultrasonic velocity and viscosity of thorium nitrate, lanthanum acetate and lanthanum chloride, it has been found that the product of adiabatic compressibility and viscosity is fairly constant over the concentration range studied. From those data the relation between ultrasonic velocity and viscosity has been derived which can explain the variation in sound velocity with the concentration.

Prakash and Srivastava,[1] from their ultrasonic velocity and viscosity measurements in aqueous

1) S. Prakash and S. P. Srivastava, *Indian J. Chem.*, **2**, 499 (1964).

solutions of silver nitrate, have explained the decrease in sound velocity with the concentration as due to the relative variation in density and viscosity parameters. These conclusions were drawn from an empirical equation obtained from the experimental data on sound velocity and viscosity in aqueous solutions of silver nitrate. Here in this present work we have again found that the variation in ultrasonic velocity with the concentration can be explained on the basis of the proposed empirical equation. No theoretical explanation of this relation can, however, be given at this time.

Experimental

Ultrasonic velocities at the frequency of 5 Mc./sec. have been measured by the light diffraction method introduced by Debye and Sears.[2)] The source of the ultrasonic waves was a generator comprising of an oscillator and a quartz transducer unit, operating at either of two frequencies, 1 Mc./sec. or 5 Mc./sec. The output of sound energy at 5 Mc./sec. was 3.5 W.; all the work was done at this frequency.

Solutions of thorium nitrate, lanthanum acetate and lanthanum chloride were prepared by dissolving pure substances (B. D. H. analar) in doubly-distilled water. The densities of these solutions were measured with the help of a relative density bottle, while the viscosities were measured with an accurate Ostwald viscometer. The errors in the measurement of the density and viscosity were 0.02 and 0.4 per cent respectively. The adiabatic compressibility, β, was calculated using the equation:

$$\beta = \frac{1}{V^2 \rho}$$

where V is the ultrasonic velocity and ρ, the density of the solution.

The probable errors involved in the measurement of sound velocity and adiabatic compressibility are 0.13 and 0.24 percent respectively.

Results and Discussion

Several workers have reported that the presence of a heavy or complex ion in a solution decreases the ultrasonic velocity. Here thorium nitrate, lanthanum acetate and lanthanum chloride all have a heavy ion; nevertheless, it is interesting to note, the ultrasonic velocity does not decrease, but instead increases linearly with the increase in concentration.

Whenever an electrolyte is dissolved in water, its compressibility is decreased. This lowering in compressibility may be attributed due to the influence of the electrostatic pressure of the ions on the surrounding water molecules, thus increasing the total internal pressure and making the solution harder to compress. The variation of adiabatic compressibility in all the cases is quite normal. It decreases regularly with the increase in concentration.

The values of the velocity, adiabatic compressibility, density and viscosity are given in Tables I, II and III.

TABLE I. THORIUM NITRATE
Temp.: 35±0.1°C

Sample No.	Concn. mol./l.	Velocity m./sec.	Adiabatic compressibility β cm²/dyne $\times 10^{12}$	Viscosity centipoise η	$\beta \times \eta \times 10^{12}$
1	0.020	1512	43.39	1.014	43.99
2	0.040	1513	42.98	1.022	43.92
3	0.050	1514	42.78	1.026	43.89
4	0.062	1515	42.45	1.030	43.72
5	0.100	1516	41.98	1.032	43.86
6	0.125	1518	41.32	1.056	43.63
7	0.250	1525	39.50	1.109	43.80
8	0.500	1532	35.47	1.230	43.61

TABLE II. LANTHANUM ACETATE
Temp.: 30±0.1°C

Sample No.	Concn. mol./l.	Velocity m./sec.	Adiabatic compressibility β cm²/dyne $\times 10^{12}$	Viscosity centipoise η	$\beta \times \eta \times 10^{12}$
1	0.006	1535.0	42.49	1.023	43.46
2	0.007	1536.7	42.46	1.024	43.49
3	0.008	1538.2	42.34	1.026	43.44
4	0.009	1541.0	42.24	1.028	43.42
5	0.010	1545.0	42.23	1.030	43.46
6	0.020	1546.6	41.93	1.038	43.45
7	0.030	1547.1	41.79	1.040	43.46
8	0.040	1548.0	41.66	1.043	43.50
9	0.050	1548.5	41.64	1.044	43.49
10	0.080	1550.2	41.45	1.052	43.46
11	0.090	1551.3	41.33	1.059	43.42

TABLE III. LANTHANUM CHLORIDE
Temp.: 30±0.1°C

Sample No.	Concn. mol./l.	Velocity m./sec.	Adiabatic compressibility β cm²/dyne $10\times^{12}$	Viscosity centipoise η	$\beta \times \eta \times 10^{12}$
1	0.042	1556.0	41.11	1.038	42.65
2	0.049	1556.5	40.96	1.043	42.74
3	0.056	1557.5	40.88	1.061	43.38
4	0.084	1564.0	40.42	1.070	43.27
5	0.112	1567.0	39.96	1.082	43.25
6	0.126	1569.0	39.53	1.096	43.31
7	0.140	1571.5	39.23	1.106	43.38

From the last column of the tables it can be seen that the product of adiabatic compressibility and viscosity is fairly constant over the concentration range studied. The average value of the constant is 43.38×10^{-12} cm²/dyne.

It follows, therefore that:

2) P. Debye and F. N. Sears, *Proc. Natl. Acad. Sci., U. S.*, **18**, 410 (1932).

$$\beta \times \eta = K \tag{1}$$

By combining the equation with the well-known equation:

$$\beta = \frac{1}{V^2 \rho}$$

we have:

$$\frac{1}{V^2 \rho} \times \eta = K \tag{2}$$

or:

$$V = \sqrt{\eta / K\rho}$$

or:

$$V = K' \sqrt{\eta / \rho} \tag{3}$$

where K' is another constant equal to $\sqrt{1/K}$. By differentiating Eq. 3 with respect to the concentration, we get;

$$\frac{1}{V_\infty} \cdot \frac{dV}{dC} = \frac{1}{2} \left[\frac{1}{\eta_\infty} \frac{d\eta}{dC} - \frac{1}{\rho_\infty} \frac{d\rho}{dC} \right] \tag{4}$$

This equation indicates that the variation in the ultrasonic velocity depends upon the magnitude of the viscosity and density parameters. Equation 4 can explain the anomalous variation in ultrasonic velocity with the concentration. Prakash and Srivastava[1] have explained the decrease in ultrasonic velocity in aqueous solutions of silver nitrate as due to the value of $1/\rho_\infty \cdot d\rho/dC$ being greater than $1/\eta_\infty \cdot d\eta/dC$.

The increase in ultrasonic velocity in thorium nitrate, lanthanum acetate and lanthanum chloride solutions can also be explained, on the basis of the above equation, as being due to the greater value of $1/\eta_\infty \cdot d\eta/dC$ than $1/\rho_\infty \cdot d\rho/dC$.

These experimental results indicate that the variation in ultrasonic velocity with the concentration is governed by two factors, the viscosity and the density of the medium.

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3) S. V. Subrahamanyam, *Trans. Faraday Soc.*, **56**, 971 (1960).
4) R. Barthel, *J. Acoust. Soc. Am.*, **260**, 227 (1954).
5) C. G. Balchandran, *Nature*, **187**, 136 (1960).