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ULTRASONIC VELOCITIES IN SOME BI-UNIVALENT ELECTROLYTES

BY C. G. BALACHANDRAN

(Department of Physics, Indian Institute of Science, Bangalore-3)

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ABSTRACT

Ultrasonic velocities and their variation with concentration up to 1 Molar have been measured for aqueous solutions of strontium iodide, lead acetate, uranyl chloride and uranyl nitrate at three different temperatures, *viz.*, 25° C., 40° C. and 60° C. From the values of the velocities the apparent molar compressibilities have been calculated. The effect of incomplete dissociation and formation of complex ions, on the slope of the apparent molar compressibility *vs.* square root of concentration curve, is discussed.

1. INTRODUCTION

An extension of the measurements of ultrasonic velocities and the determination of apparent molar compressibilities therefrom, to the case of ions of large size is desirable. With this object in view, ultrasonic velocities, densities and apparent molar compressibilities of aqueous solutions of strontium iodide, lead acetate, uranyl chloride and uranyl nitrate have been determined for the first time and are reported in this paper.

2. EXPERIMENTAL DETAILS

The Bachem-Hiedemann (1936) method of secondary interferences involving the photography of the interference pattern formed by the lines of convergence was employed for the determination of sound velocities in solutions of strontium iodide and lead acetate. The fringe system was made as sharp and parallel as possible by adjusting a parallel reflector facing the radiating quartz crystal. The average fringe width of 50 fringes was measured from the photograph using a comparator. The cell containing the salt solution was maintained successively at different temperatures, *viz.*, 25° C., 40° C. and 60° C. by circulating water from a thermostatically controlled water-bath. The temperature was maintained constant to within ± 0·1° C. upto 60° C. The actual temperature of the ultrasonic cell under control was determined by a thermometer attached to it. Velocity determinations were as accurate as possible by taking the photograph of the interference pattern for distilled water on the same photographic plate. The frequency of the electron-coupled 807 valve oscillator generating the ultrasonic waves was determined by a BC-221 heterodyne wavemeter.

In the case of uranyl salts whose solutions have a strong yellow colour an ultrasonic interferometer was used for the determination of sound velocities. Perfect temperature control could be obtained in this case as well by circulating water around the interferometer cell from the thermostatically controlled water-bath. The velocity determinations were made very accurately by measuring 50 half-wavelengths. The frequency of the ultrasonic waves was checked before and after every measurement.

The materials used were very pure Merck products. Uranyl salts were recrystallized from the original samples. Extreme care was taken while preparing the solutions to prevent contamination. Double distilled water was used for the preparation of the solutions especially to avoid hydrolysis of the salt solutions.

Densities of the solutions for every concentration and temperature were determined accurately using a specific gravity bottle. Using the formula $\beta = 1/v^2d$, where v is the ultrasonic velocity in metres/second and d the density in gm. c.c., β the adiabatic compressibility was calculated. Apparent molar compressibilities were calculated according to the formula

$$\phi(k) = \frac{1000\,\beta}{c} - \frac{\beta_1}{d_1}\left(\frac{1000\,d}{c} - M_2\right),$$

where β_1 is the adiabatic compressibility of water at a particular temperature, d_1 the density of water at the same temperature, c the salt concentration in mols/litre and M_2 the molecular weight of the solute.

3. RESULTS

The Tables (I to IV) give the measured values of ultrasonic velocity and density and the calculated values of adiabatic compressibility. Graphs showing the variation of apparent molar compressibility with square root of concentration are also given (Figs. 1 to 4).

TABLE I. *Strontium Iodide*

No.	Concentration in moles per litre	Temperature in deg. C.	Velocity in metres per sec.	Density in gm./c.c.	Adiabatic Compressibility in cm.^{2}/dyne $\times 10^{12}$
1	0·1250	25	1497	1·0336	43·172
2	0·2500	25	1494	1·0681	41·946
3	0·3600	25	1491	1·0996	40·908
4	0·5000	25	1487	1·1396	39·685
5	0·8000	25	1481	1·2245	37·233
6	1·0000	25	1478	1·2811	35·733
1	0·1250	40	1523	1·0282	41·930
2	0·2500	40	1518	1·0624	40·848
3	0·3600	40	1513	1·0935	39·949
4	0·5000	40	1505	1·1330	38·915
5	0·8000	40	1495	1·2168	36·770
6	1·0000	40	1488	1·2727	35·487
1	0·1250	60	1543	1·0187	41·231
2	0·2500	60	1536	1·0524	40·275
3	0·3600	60	1528	1·0834	39·533
4	0·5000	60	1517	1·1222	38·722
5	0·8000	60	1498	1·2046	36·994
6	1·0000	60	1486	1·2597	35·950

TABLE II. *Lead Acetate*

No.	Concentration in moles per litre	Temperature in deg. C.	Velocity in metres per sec.	Density in gm./c.c.	Adiabatic Compressibility in cm.^{2}/dyne $\times 10^{12}$
1	0·1177	25	1497	1·0215	43·680
2	0·2500	25	1489	1·0519	42·878
3	0·4000	25	1481	1·0869	41·947
4	0·5161	25	1472	1·1148	41·398
5	0·7000	25	1461	1·1577	40·467
6	1·0000	25	1445	1·2277	38·990
1	0·1177	40	1524	1·0177	42·307
2	0·2500	40	1516	1·0481	41·514
3	0·4000	40	1505	1·0834	40·751
4	0·5161	40	1496	1·1112	40·211
5	0·7000	40	1483	1·1542	39·395
6	1·0000	40	1463	1·2242	38·164
1	0·1177	60	1545	1·0090	41·519
2	0·2500	60	1539	1·0370	40·714
3	0·4000	60	1527	1·0715	40·025
4	0·5161	60	1516	1·0992	39·584
5	0·7000	60	1500	1·1426	38·898
6	1·0000	60	1475	1·2134	37·380

TABLE III. *Uranyl Chloride*

No.	Concentration in moles per litre	Temperature in deg. C.	Velocity in metres per sec.	Density in gm./c.c.	Adiabatic Compressibility in $cm.^2/dyne \times 10^{12}$
1	0·1000	25	1495	1·0260	43·608
2	0·2000	25	1490	1·0541	42·731
3	0·3000	25	1481	1·0840	42·059
4	0·5000	25	1473	1·1393	40·454
5	0·7000	25	1468	1·1929	38·890
6	1·0000	25	1461	1·2732	36·796
1	0·1000	40	1520	1·0224	42·334
2	0·2000	40	1515	1·0503	41·537
3	0·3000	40	1505	1·0800	40·879
4	0·5000	40	1495	1·1349	39·424
5	0·7000	40	1487	1·1881	38·065
6	1·0000	40	1477	1·2678	36·157
1	0·1000	60	1547	1·0099	41·375
2	0·2000	60	1539	1·0378	40·683
3	0·3000	60	1525	1·0695	40·205
4	0·5000	60	1514	1·1224	38·860
5	0·7000	60	1505	1·1756	37·555
6	1·0000	60	1489	1·2555	35·925

TABLE IV. *Uranyl Nitrate*

No.	Concentration in moles per litre	Temperature in deg. C.	Velocity in metres per sec.	Density in gm./c.c.	Adiabatic Compressibility in $cm.^2/dyne \times 10^{12}$
1	0·1000	25	1493	1·0296	43·55
2	0·2000	25	1488	1·0610	42·55
3	0·3000	25	1484	1·0950	41·45
4	0·5000	25	1478	1·1591	39·50
5	1·0000	25	1468	1·3180	35·20
1	0·1000	40	1524	1·0250	42·00
2	0·2000	40	1515	1·0596	41·11
3	0·3000	40	1510	1·0913	40·19
4	0·5000	40	1502	1·1547	38·39
5	1·0000	40	1486	1·3129	34·49
1	0·1000	60	1544	1·0163	41·28
2	0·2000	60	1536	1·0490	40·41
3	0·3000	60	1532	1·0789	39·49
4	0·5000	60	1525	1·1388	37·76
5	1·0000	60	1497	1·2966	34·62

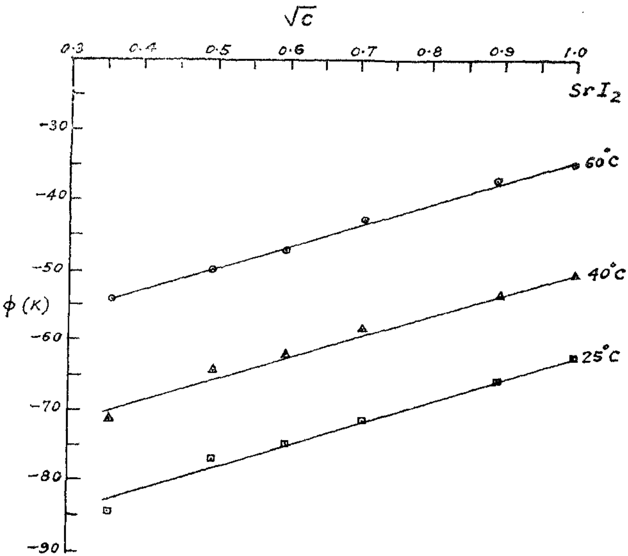
√c
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
SrI2
-30
-40
-50
-60
-70
-80
-90
φ (K)
60°C
40°C
25°C

FIG. 1

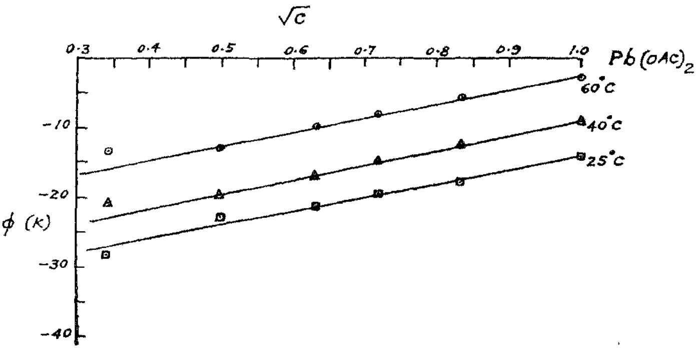
√c
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
Pb(OAc)2
-10
-20
-30
-40
φ (K)
60°C
40°C
25°C

FIG. 2

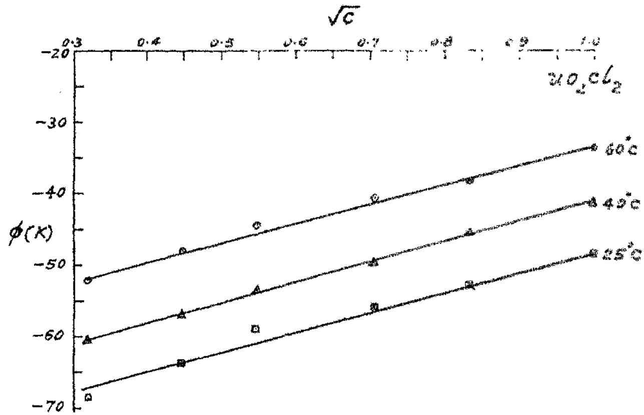
√C
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
−20
−30
−40
−50
−60
−70
φ(K)
UO₂Cl₂
60°C
40°C
25°C

FIG. 3

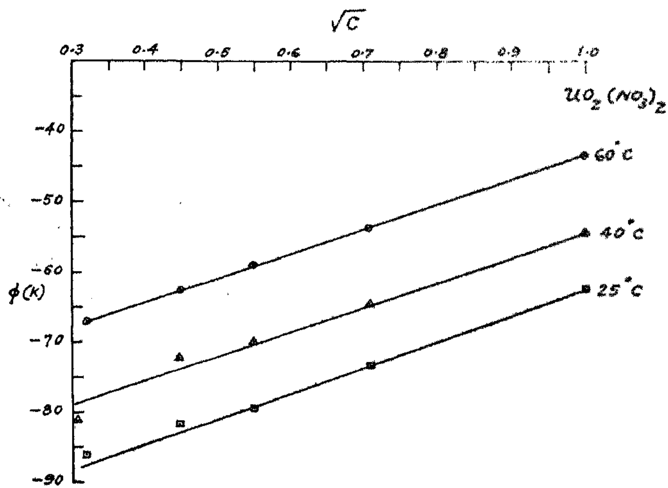
√C
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
−40
−50
−60
−70
−80
−90
φ(K)
UO₂(NO₃)₂
60°C
40°C
25°C

FIG. 4.

4. Discussion

The peculiar feature of the results is that the ultrasonic velocity always remains less than that in water and goes on decreasing with increasing concentration in all the cases up to the highest concentration studied. So far only two salts are known to behave in this rather anomalous fashion. They are potassium iodide and lead nitrate (Freyer, 1931; Barthel, 1954). Such a decrease has been explained by Barthel (1954) as due to heaviness of the ions which decrease the velocity of the Brownian motion of these particles and consequently the sound velocity. The present results support this hypothesis as heavy ions are present in all these salts.

However, this does not in any way affect the course of the apparent molar compressibility *vs.* square root of concentration curves of these salts. It is found that these curves are all linear, so that the behaviour in these cases is not different from normal, *e.g.*, the case of potassium chloride, sodium chloride, etc. It is of interest, however, to compare the magnitudes of the slopes with the Debye-Huckel theoretical values. The individual behaviour of these salt solutions can now be discussed.

Strontium Iodide.—The main feature of the experimental data is that the velocity decreases with increasing concentration up to 1 Molar at all temperatures and is always less than that of water. However, the adiabatic compressibility is always less than that of water. This perhaps may be due to the presence of heavy ion like I^- – as this feature is common to all the iodides that have been studied. The curves between apparent molar compressibility and square root of concentration show a linear variation. The slope is of the same order as found from theory for 1 : 2 valent electrolytes (theoretical value $32 \cdot 6 \times 10^{-10}$; experimental value $31 \cdot 2 \times 10^{-10}$).

Lead Acetate.—This is one of the very few lead salts that is soluble in water up to fairly high concentrations and is stable and hence has been selected for these measurements. Here also the velocity is always less than that in water and goes on decreasing with increasing concentration up to the highest concentration studied. The variation of apparent molar compressibility with square root of concentration is linear. Its slope, however, is very much less than the theoretical value (theoretical value $32 \cdot 6 \times 10^{-10}$; experimental value $19 \cdot 0 \times 10^{-10}$). The apparent molar compressibility (which is always negative) has a numerically smaller value at infinite dilution.

A possible factor responsible for this anomalous behaviour in the apparent molar compressibility curves may be the existence of a large fraction of undissociated ions. This argument is supported by the evidence from X-ray diffraction data. Prins (1935) found that the intensity of the X-ray diffraction ring in aqueous solutions of lead acetate did not show any pronounced maxima and minima and also it did not decrease markedly as the diffraction angle approached zero. He postulates the existence of a large fraction of undissociated molecules with a " gaseous distribution" as in the case of cadmium iodide in water. From electrical conductivity measurements of lead acetate in acetic acid it is seen that this salt behaves as a typical weak base (Davidson *et al.*, 1942).

Uranyl Chloride.—In this case also there is an anomalous variation of sound velocity with concentration in that the velocity goes on decreasing with increasing concentration and is always less than that of water. The adiabatic compressibility values are normal. The apparent molar compressibility varies linearly with the square root of concentration. But the slope of the linear plot is much less than the value predicted from theory (theoretical value $32 \cdot 6 \times 10^{-10}$; experimental value $26 \cdot 6 \times 10^{-10}$). The decreased slope is probably due to the existence of intermediate complexes in this salt solution. The existence of such complexes, [illegible] at high concentrations, has been suggested from calculations of activity coefficient. In concentrated solutions the activity coefficient of uranyl chloride is actually less than that of magnesium chloride suggesting that uranyl chloride forms complex salts (Robinson and Lim, 1951). In dilute solutions it is only slightly above that of concentrated magnesium chloride in a plot between log γ and concentration.

Uranyl Nitrate.—The velocity change is anomalous as in the previous three cases. The compressibilities are normal. The apparent molar compressibility varies linearly with the square root of concentration and the slope is also of the predicted order (theoretical value $32 \cdot 6 \times 10^{-10}$; experimental value $34 \cdot 0 \times 10^{-10}$). So it can be said that except for the anomalous variation of velocity with concentration this salt behaves normally at all concentrations and temperatures and obeys Debye-Huckel law. There is considerable evidence to indicate that uranyl nitrate in aqueous solutions is a strong electrolyte, almost completely ionized. X-ray evidence also clearly (Prins, 1935) supports the above view in that the X-ray diffraction pattern of saturated solution of this salt consists mainly of a pronounced ring which shifts to smaller angles and becomes fainter with dilution, indicating a more or less regular arrangement of the ions in the liquid. Activity coefficients (Robinson *et al.*, 1942) are very high as found in the case of magnesium chloride and zinc iodide indicating that there is practically no intermediate ion formation.

In conclusion the salient features of the experimental results brought out by the above studies on electrolytes can be summarized:-

1. While in general sound velocities in electrolytes are greater than that of water and increase with increasing concentration at all temperatures, the present experiments reveal the opposite type of behaviour in all the cases studied, *i.e.*, a decrease in sound velocity with increasing concentration the values being always less than that of water.

2. It is also a striking feature that the velocity decrease is always associated with the presence of heavy ions like I^{--}, Pb^{++}, U^{++}, etc. So it is probable that a correlation exists between the two factors. It has been suggested by Barthel, that in the case of heavy ions the velocity of Brownian motion is much less and this

may result in a decrease in velocity, Brownian motion being regarded as one of the factors that contribute to the sound velocity.

3. It is noteworthy however that the adiabatic compressibilities are quite normal in all these cases, being always less than that of water at all concentrations and temperatures.

4. One more striking feature is that in spite of anomalous variation in sound velocity a linear variation of apparent molar compressibility with square root of concentration is found in all the cases as predicted by the Debye-Huckel theory.

5. The slopes of the apparent molar compressibility *vs.* square root of concentration curves and the values of the apparent molar compressibility at infinite dilution do not show any marked correlation with the decrease in velocity with increasing concentration.

6. On the other hand these properties seem to be related more with the state of dissociation of the electrolytes and the existence of complex ions.

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