# Sound Velocity in Aqueous Solutions of Lead Nitrate and Ammonium Iodide

Otohiko Nomoto*,** and Harumi Endo*

* *Department of Applied Physics, Defence Academy, Yokosuka*

** *Kobayashi Institute of Physical Research, Kokubunji, Tokyo*

(Received June 3, 1970)

The sound velocity in aqueous solutions of $NH_4I$ and $Pb(NO_3)_2$ is investigated in relation to the temperature and the concentration. In both solutions the $V(T)$ curves show maxima $V_p$ at the peak temperature $T_p$, the $T_p$ shifting to a lower temperature with an increase in the concentration. While the shift of $T_p$ is sensibly linear with the concentration for $Pb(NO_3)_2$, the curve for $NH_4I$ is almost constant up to 25 wt%, though it decreases linearly above this concentration. This corresponds to the rather abrupt change in the degree of dissociation obtained from the conductivity data. The constancy of $T_p$ below 25 wt% is tentatively explained on the basis of Danford and Levy's X-ray diffraction study which concluded that $NH_3$ is included in cavities of the water framework and that the framework molecules are partially replaced by $NH_3$.

Generally speaking, the sound velocity ($V$) in a solution is dependent on both the temperature ($T$) and the concentration ($C$); *i. e.*, $V=V(T,C)$. No systematic study of the sound velocity in aqueous electrolyte solutions has, however, been made over a wide range of concentration and temperature, except for the studies of Tamm *et al.*[1] and Marks.[2,3] They found that the $V(T)$-curve at a constant concentration in electrolyte solutions exhibits its peak velocity ($V_p$) at a definite temperature — the peak temperature ($T_p$) — for each concentration, such as in the $V(T)$ curve of pure water. The $V(T)$ curve shifts upwards with an increase in the concentration, while there is a shift of $T_p$ towards a lower temperature at the same time. This shift of $T_p$ is linearly dependent on the concentration (molarity).

Reviews[4-7] of the water structure have appeared elsewhere. A water model closely related to a slightly-expanded ice-1 lattice is proposed by Samoilov[8,9] and supported by Danford and Levy[10] on the basis of their X-ray diffraction studies. In this structure, each network molecule is tetrahedrally surrounded by an average of *ca.* 4.4 first neighbors.[11] The structure of this network is very bulky, with space within the framework of molecules in the tetrahedral coordination sufficiently large to accommodate additional water-molecules, and while these spaces—cavities— are not occupied in solid ice-1, about half the cavities in water are occupied by interstitial molecules which interact with the network by less directional, but by no means negligible, forces (Danford and Levy[10]).

As Debye[12] pointed out, the electrostatic field of the ions exerts an electrostrictive effect on the surrounding water molecules; this electrostatic pressure has the same effect as the application of an external pressure and diminishes the volume as well as the compressibility of water molecules. In general, the addition of an electrolyte to water results in a lowering of the peak temperature because of the destruction of the cluster by the solvation of the ions. In many electrolytes, the sound velocity increases as compared with that of pure water. However, there are electrolytes which exhibit a decrease in the sound velocity with an increase in the concentration, such as LiI, NaI, KI, $NH_4I$, $AgNO_3$[13]; CsCl, CsBr[14]; $Pb(NO_3)_2$[15]; $ZnBr_2$, $ZnI_2$[16]; $UO_2Cl_2$, $UO_2(NO_3)_2$, $SnI_2$, $(CH_3COO)_2Pb$[17]; $CdBr_2$[18]; $CdI_2$[19]; $TlNO_3$[20]; and RbBr, RbI.[21]

The purpose of the present study is to clarify the molecular mechanism of sound propagation in aqueous electrolyte solutions in connection with the accepted molecular structure of water and aqueous solutions, and to clarify the dissolved state and the properties of ions in aqueous solutions. We studied ammonium iodide and lead nitrate solutions, both electrolytes showing a decrease in the sound velocity with an increase in the concentration.

## Experimental

*Apparatus.* The sound velocity is measured with a crystal-controlled ultrasonic interferometer equipped with a 5 MHz X-cut quartz transducer. The accuracy of this method depends on the number of standing waves counted. We counted one hundred standing waves. The interferometer cell is immersed in an oil bath controlled within ±0.1°C at moderate temperatures and within ±0.4°C at higher tem-

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[2] G. W. Marks, *J. Acoust. Soc. Amer.*, **31**, 936 (1959).

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[10] M. D. Danford and H. A. Levy, *J. Amer. Chem. Soc.*, **84**, 3965 (1962).

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[12] P. Debye, Festschrift H. Zangger; II. Teil Verlag Rasher & Co., Zürich, (1935), p. 877.

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[17] W. P. Mason, "Physical Acoustics" Part II-A, Academic Press, New York, London (1965), p. 355.

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[20] B. Lunden, *Z. Physik. Chem.*, **192**, 345 (1943).

[21] S. V. Subrahmanyam, *Z. Angew. Physik*, **15**, 352 (1963).

peratures. The dominant cause of error in sound velocity measurement is temperature fluctuations. The temperature coefficient of the sound velocity in usual aqueous solutions being *ca.* −2——3 m/sec/deg at room temperature, the estimated overall error in this study amounts to ±0.2 m/sec at moderate temperatures and ±1.5 m/sec at higher temperatures. Temperature measurement is made with a thermistor. The sound velocity is measured in terms of its dependence on the temperature for various electrolyte concentrations.

*Materials.* Lead nitrate and ammonium iodide, special reagent grade, are both recrystallized from water. Salts are prepared by maintaining the crystals at 95°C for two weeks under a reduced pressure of *ca.* 1 mmHg. After purification, ammonium iodide completely turned into colorless salt.

## Results and Discussions

The $V(T)$-curves at various concentrations for lead nitrate and ammonium iodide aqueous solutions over the temperature range of 20—100°C are shown in Figs. 1 and 2 respectively. Measurements of the concentration dependence of the sound velocity $V(C)$ under a constant temperature in $Pb(NO_3)_2$ and $NH_4I$ aqueous solutions has been reported, but there have, to our knowledge, been no measurements of the temperature dependence of the sound velocity. It is observed that the height of $V(T)$-curves of an aqueous solution of $Pb(NO_3)_2$ or $NH_4I$ is lower than that of water and that the curves are displaced towards a lower temperature with an increase in the concentration in such a way as to maintain the parabolic shape of the $V(T)$-curve of water.

All kinds of somewhat dilute aqueous solutions, regardless of whether they are ionic[22,23] or non-ionic[24,25] substances, have parabolic curves like that of water. When a solute is added to water, the statistical equilibrium among different species is displaced and there is a partial destruction of the clusters; the decrease in the cluster by the solutes causes the peak temperature to become lower as compared with that of pure water.

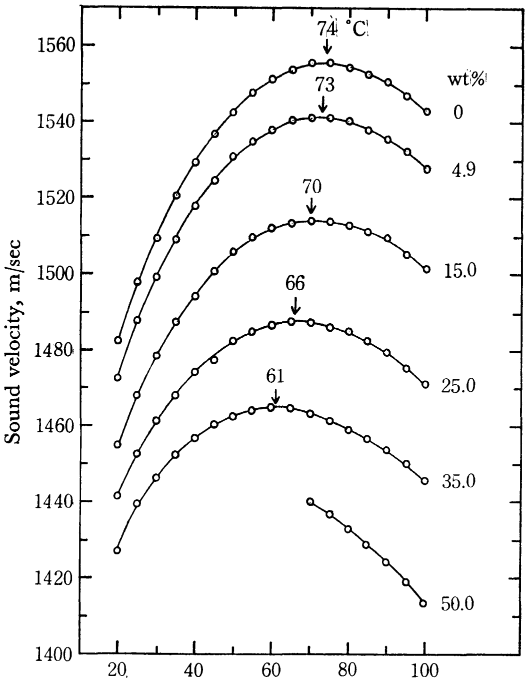

Fig. 1. Sound velocity of lead nitrate aqueous solutions. Arrows show the peak temperature.

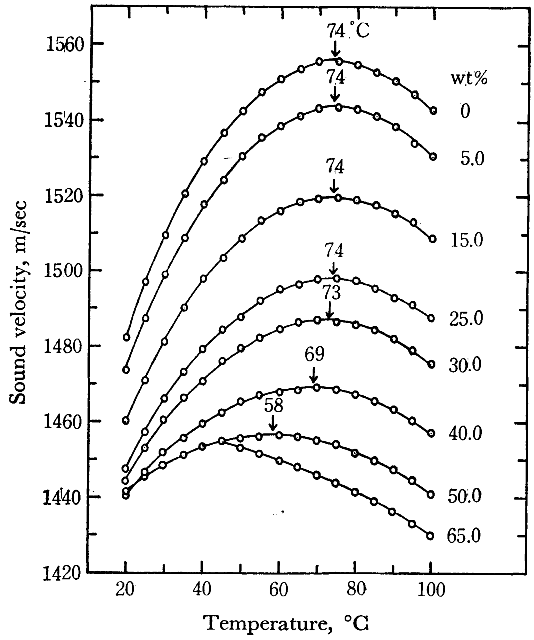

Fig. 2. Sound velocity of ammonium iodide aqueous solutions. Arrows show the peak temperature.

The origin of an anomalous temperature dependence of the sound velocity in water and aqueous solutions can be sought in the structure of water. The cluster-part of water decreases with an increase in the temperature, resulting in a decrease in the structural compressibility. The increase in the molecular distance with the temperature-rise is accompanied by an increase in the ordinary compressibility due to the compression of the free space between non-associated water molecules. These opposite effects lead to a minimum of the compressibility at an intermediate temperature, or to the maximum of the sound velocity at a slightly different temperature.

The plot of the peak temperature against the concentration—$T_p(C)$—gives information on the water structure and the dissolved state, and also on the properties of ions in aqueous solutions. The relation between the peak temperature and the concentration has been extensively studied for various sulfates and hydroxides (*cf.* Marks[2,3]). In these solutions, the sound velocity rises with an increase in the concentration. On the other hand, the peak temperature ($T_p$) decreases with

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[22] W. Schaaffs, Landolt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenshaften und Technik Gruppe II, Band 5, "Molekularakustik," Springer-Verlag, Berlin, Heidelberg, New York (1967), pp. 109—126.

[23] J. Saneyoshi, K. Kikuchi, and O. Nomoto, "Tyoonpa Gizitu Binran," Nikkan Kogyo Sinbunsya, Tokyo (1966), pp. 1253—1258.

[24] O. Nomoto and H. Endo, This Bulletin, **43**, 2718 (1970).

[25] Nippon Kagaku Kai, "Jituken Kagaku Kouza," 5, Maruzen, Tokyo (1958), pp. 433—448.

an increase in molarity ($m$) along a straight line:

$$T_p = (T_p)_0 - km, \quad \text{where } (T_p)_0 = 74°\text{C}$$

with a common negative slope ($k$) for $Li_2SO_4$, $Na_2SO_4$, and $K_2SO_4$. Here $(T_p)_0$ is the peak temperature for water. Also, the $V(T)$-curves are nearly common for these three salts. The $T_p(m)$-curves for the other salts are straight lines, with a different slope for each salt. Marks concluded that the above-mentioned three salts affect the compressibility and the density of water in such a way that the maximum sound-velocity-changes ($\Delta V_p$) with the concentration become nearly the same. This is evidence that the ionic charge is the determining property rather than the ionic size in electrolyte solutions. We have studied the shift of $T_p$ with the concentration in organic aqueous solutions, and, by ascribing the $T_p$ to the destruction of the water structure, we have found that, regardless of the kind of organic substance, there exists a simple linear relation between $T_p$ and the geometical surface area of the solute.[24]

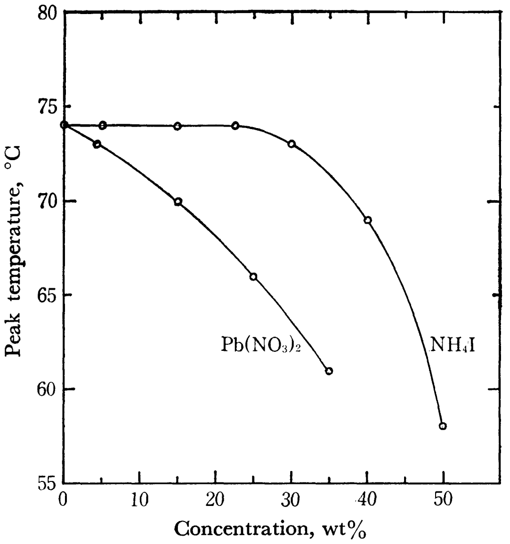

**Fig. 3.** Peak temperature in dependence of concentrations for lead nitrate and ammonium iodide aqueous solutions.

Figure 3 shows the $T_p(C)$-curves, with the weight-% as the abscissa. As may be seen, the peak temperature of the $Pb(NO_3)_2$ solution decreases linearly with the concentration. On the other hand, the behavior in the $NH_4I$-solution is very different from that in solutions of the other salts, such as sulfates, hydroxides, and $Pb(NO_3)_2$. The peak temperature in the $NH_4I$-solution does not change with the concentration up to *ca.* 25 wt%, with the $T_p$-value of water maintained at 74°C. Above this concentration, the $T_p$ decreases as in other electrolyte-solutions.

The origin of the anomalous concentration dependence of the peak temperature in an $NH_4I$ aqueous solution is to be explained on the basis of a slightly-expanded ice-1-model[8] of the water structure and the peculiarity of the dissolved state of $NH_4^+$ and $I^-$ ions in an aqueous solution.

There are a number of parameters pertaining to the properties and dissolved state of ions in aqueous solutions, the hydration number being one such parameter. We have many experimental methods[25] for determining the hydration number of ions in aqueous solutions, such as mobility, entropy of mixing, and diffusion. Also, the hydration number has been acoustically determined from the sound velocity by many authors. It must be particularly emphasized, as regards the acoustically-determined hydration number, that the observed quantity is the overall bulk compression of the solution, and that no distinction between the effects to be ascribed to the nearest neighbors of the ions and the far distant molecular species as clusters of water, *etc.*, can be made. The so-called "hydration number," as determined by the acoustical method, is based on a model assuming incompressible hydrated water molecules and non-affected surrounding water. The physical interpretation of the acoustic hydration number is, however, rather the net destruction of the water structure. The hydration numbers for the ions, as obtained by various experimental methods, are remarkably different[26,27] from one another. The values obtained from the sound-velocity data are usually higher than those obtained by the other methods. Nevertheless, the acoustically-determined hydration number is a significant parameter for the study of the properties and the dissolved state of ions in aqueous solutions. Table 1 shows the hydration numbers for $(NH_4^+ + I^-)$ and $(Pb^{2+} + 2NO_3^-)$ as obtained by acoustical means. Usual ions have acoustical hydration numbers between 5—16.[26] As may be seen in Table 1, $NH_4I$ ($NH_4^+$ plus $I^-$) has exceptionally small hydration numbers. Therefore, it may be concluded that $NH_4^+$ and $I^-$ ions do not destroy the water structure so much. Now we see from Fig. 3 that the peak temperature is not shifted, and that the water structure in the $NH_4I$-solution is not destroyed, for concentrations up to *ca.* 25 wt%. We reached the conclusion that the $NH_4^+$ and $I^-$ ions can fill in the cavity positions in an expanded ice-1 structure of water without any serious destruction of the molecular arrangements. The $NH_4^+$ ion can replace the network-point of water molecules, too. Since the ions packed in the cavities serve only to expand the lattice, without destroying the water structure, the shift of $T_p$ is expected to be small.

TABEL 1. THE HYDRATION NUMBER FOR VARIOUS IONS

| Ion | Author | The other |
|---|---|---|
| $NH_4^+$ | $NH_4I$ 3.0 | 2.0[13] |
| $I^-$ | | 0.2,[13] 0.1[27] |
| $Pb^{2+}$ | $Pb(NO_3)_2$, 10.8 | |
| $NO_3^-$ | | 2.0,[13] 1.1[27] |

We have reported that, in the case of aqueous organic solutions, the shift of $T_p$ is nearly proportional to the total surface area of the solutes. The shift of $T_p$ is discernible for $NH_4I$ solutions in the concentration range higher than *ca.* 30 wt%. This is presumably to be ascribed to the increase in neutral $NH_4I$ molecules in this concentration range, as is also evidenced by

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[26] R. Robinson and R. Stokes, "Electrolyte Solutions," Butterworths, London (1959) p. 62.

[27] 15th-Tyoonpa Kenkyukai Siryo, T. Yasunaga, Denki Tusin Gatukai (1964).

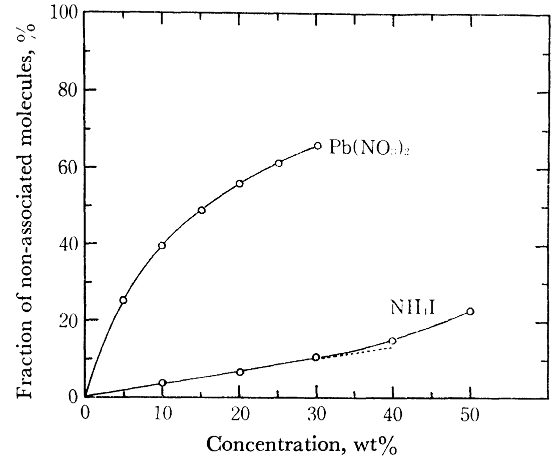

Fig. 4. Fraction of non-associated molecules in dependence of concentrations for lead nitrate and ammonium iodide aqueous solutions.

the change in the conductivity.[28] The fraction of non-dissociated solutes, as obtained from the conductivity data, is also indicated in Fig. 4. The curve shows a rather abrupt turn at 30 wt%. Both the turn of the $T_p$-curve and that of the degree of dissociation in the $NH_4I$ aqueous solution at nearly the same concentration may correspond to the transformation of the properties and the dissolved state of ions in aqueous solutions.

The model used here is strongly supported by the results of investigations of water,[10,29] an aqueous ammonia[30] solution, and aqueous ammonium halide[31] solutions by the X-ray diffraction method (*cf.* also aqueous tetra-*n*-butylammonium fluoride[32]). That is, it is concluded by the X-ray method that the ammonia and ammonium ions can replace the water molecule in the network of the expanded ice-1 structure and also fill up the cavities in this bulky structure. It has been stated that, in pure water,[10] the ratio of the framework to the free water molecules is 4 : 1, and that half the cavities in framework are filled by free water molecules. In the case of the water-ammonia[29] system of 28 mol%, it has been stated that 76% of the available cavities are occupied by ammonia molecules. Although the X-ray analysis may not be able to distinguish between the free single-water molecules and the single-water molecules filling in the cavities of the frameworks of the clusters, the X-ray results[30] do not contradict the present result.

We can see from Fig. 3 that $T_p$ decreases in a $Pb(NO_3)_2$-solution sensibly and linearly with an increase in the concentration. Also, the non-dissociated fraction of $Pb(NO_3)_2$ molecules, as obtained from the conductivity[33] data, increases more rapidly than $NH_4I$ with the concentration (*cf.* Fig. 4). The large hydration number of $Pb(NO_3)_2$ may be the reason why the ions do not fill in the cavities in water frameworks, but destroy the framework from the beginning.

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[28] J. Bartels *et al.*, Landolt-Börnstein, Zahlenwerte und Funktionen aus Physik. Chemie. Astronomie. Geophysik und Technik. II Band, 7 Teil "Electrische Eigenschaften" Springer-Verlag, Berlin, Göttingen, Heidelberg, (1960), p. 39.

[29] A. Narten, M. Danford, and H. Levy, *Discuss. Faraday Soc.*, **43**, 97 (1967).

[30] A. Narten and S. Lindenbaum, *J. Chem. Phys.*, **51**, 1108 (1969).

[31] A. Narten, *J. Amer. Chem. Soc.*, **74**, 765 (1970).

[32] A. Narten, *J. Chem. Phys.*, **49**, 1692 (1968).

[33] Landolt-Börnstein II Band, 7 Teil "Elektrische Eigenschaften," Springer-Verlag, Berlin, Göttingen, Heidelberg (1960), p. 119.