

## PROPAGATION OF ELASTIC WAVES THROUGH ELECTROLYTIC SOLUTIONS\*

By A. K. DUTTA

AND

B. B. GHOSH

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**ABSTRACT** The change of supersonic velocity and hence the change of compressibility of different electrolytic solutions with concentration have been studied by previous workers from the standpoint of the ionic theory of Debye. They have so far observed only a rise of supersonic velocity with concentration and have explained minor characteristics of the curve. It has been shown here that heavy alkali halides show at first a decrease of velocity with concentration and then an increase of velocity. This effect is enhanced at higher temperatures. Inasmuch as this behaviour is of opposite nature to the general behaviour of the other electrolytes, the compressibility-concentration relationship bears a close relationship with the viscosity-concentration relationship. These similarities have been critically considered.

Two papers on the variation of supersonic velocity with the concentration of electrolytic solutions have drawn some attention. One of them by Szalay<sup>1</sup> gives measurements of supersonic velocity on LiCl, NaCl, KCl, KBr, Li<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, ZnSO<sub>4</sub>, CdSO<sub>4</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. He has observed that the velocity increases with the concentration linearly. The rate of increase of velocity seemed to have no relationship with the valency of the ions. Considering the respective densities he observed that the compressibility decreases with the concentration in electrolytes. He has, however, tried to show that the percentage decrease of compressibility  $d\beta/\beta$  at any concentration falls within definite ranges according to the concentration and the ionic valency.

Falkenhagen and Bachem<sup>2</sup> have tried to show in another paper the relationship of the variation of compressibility with concentration from the standpoint of the ionic theory of Debye and Falkenhagen. From the experimental data on the variation of supersonic velocity with concentration and the densities at the corresponding concentrations, they worked out the compressibilities of different salts at different concentrations and plotted the respective curves. These curves show a slight inclination towards the axis. Thus the curves are of the type  $\beta = \beta_0 + A'C + B'C^{3/2}$  where  $A'$  is large and negative and  $B'$  is of a smaller order and positive. In essence, Falkenhagen and Bachem have compared the coefficient  $B'$  with a constant derived from the ionic theory, the

larger coefficient  $A'$ , which determines the general slope of the curves has been left out of consideration. The basis of comparison in Falkenhagen and Bachem's work is as follows:—

The apparent molar compressibility of a solution  $\phi(k)$  can be determined when the concentration, the densities and compressibilities of the solvent and the solution are known. Thus the apparent molar compressibility is given by the relationship

$$\phi(\bar{k}_2) = - \frac{(\delta V / \delta p) - (-\delta V_1 / \delta p)}{n_2}$$

where  $V$  and  $V_1$  are the volumes of solution and solvent and  $n_2$  is the number of moles dissolved,

or

$$\phi(\bar{k}_2) = \frac{\beta V - \beta_1 V_1}{n_2}$$

where  $\beta$  and  $\beta_1$  are the compressibilities of the solution and solvent,

or

$$\phi(\bar{k}_2) = \beta \frac{1000}{c} - \beta_1 \left( \frac{1000d}{c} - M_2 \right)$$

where  $M_2$  is the molar wt. of the solute. Hence knowing  $\beta$ ,  $\beta_1$ ,  $d$ ,  $d_1$ ,  $c$ ,  $M_2$ ,  $\phi(\bar{k}_2)$  can be experimentally determined and a graph of  $\phi(\bar{k}_2)$  against  $c$  or  $\sqrt{c}$  can be drawn.

Now,  $\phi(\bar{k}_2)$  is related with the partial molar compressibility  $\bar{k}_2$  which varies with the concentration according to a definite law determined by the ionic theory of Debye and Falkenhagen.

Thus  $\bar{k}_2$ , the partial molar compressibility

$$- \frac{\partial}{\partial n_2} \left( - \frac{\partial V}{\partial p} \right) = \frac{\partial}{\partial n_2} (\beta V) = \frac{\partial}{\partial n_2} n_2 \left[ \phi(\bar{k}_2) \right]$$

since  $\beta_1$  and  $V_1$  corresponding to the solvent are constants.

or

$$\begin{aligned} \bar{k}_2 &= \phi(\bar{k}_2) + n_2 \frac{\delta \phi(\bar{k}_2)}{\delta n_2} \\ &= \phi(\bar{k}_2) + c \frac{\delta \phi(\bar{k}_2)}{\delta c} \end{aligned}$$

If  $\bar{k}_2$  is of the form  $a + m\sqrt{c} = a + \frac{3}{2}b\sqrt{c}$ , it can be also written as

$$\bar{k}_2 = a + b\sqrt{c} + c \frac{b}{2\sqrt{c}} = (a + b\sqrt{c}) + c \frac{\delta}{\delta c} (a + b\sqrt{c}).$$

Comparing the two equations for  $\bar{k}_2$  thus obtained one gets,

$$\phi(\bar{k}_2) = a + b\sqrt{c} \quad \text{when} \quad \bar{k}_2 = a + \frac{3}{2}b\sqrt{c}.$$

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Now, according to ionic theory, an expression for  $k_2$  can be obtained in the form

$$k_2 = k_2^0 - \sum v_i RT \frac{\delta}{\delta p} (\beta - \beta_1) + \frac{a (\sum v_i z_i^2)^{\frac{3}{2}}}{D^{\frac{3}{2}} T^2} \sqrt{c},$$

where the second term is negligible compared with the third, so that  $k_2$  is roughly of the form  $k_2 = a + m \sqrt{c}$  where  $m$  is the constant from the ionic theory and can be calculated when the valency of the electrolyte is known. This value of ' $m$ ' derived from the ionic theory can be compared with the coefficient (3.2)  $b$  in the equation for partial compressibility, where  $b$  is obtained from the graph of apparent molar compressibility drawn against  $\sqrt{c}$ .

In the results calculated by Falkenhagen and Bachem, the values are of the same order. But as Bachem<sup>3</sup> points out in a later paper, the coefficient of the same valency does not remain constant as demanded by theory.

However, since

$$\psi(k_2) = \frac{-\delta V / \delta p - \delta V_1 / \delta p}{n_2} = a + b \sqrt{c}$$

it is apparent that in the relationship  $\beta = \beta_0 + A'C + B'C^{\frac{3}{2}}$  the coefficient  $A'$  is composed of the coefficient ' $a$ ' in the equation for apparent molar compressibility and the coefficient  $B'$  is composed of the coefficient ' $b$ ' in the former equation. As we have mentioned previously that in the equation for compressibility  $A'$  is large and of a higher order than  $B'$ , we compare by the method of Falkenhagen and Bachem a secondary effect on the course of the compressibility curve, and the general nature of the variation of compressibility with concentration remains beyond the scope of the ionic theory alone. This remains yet an open problem.

It was considered by us that the compressibility of a liquid medium or a solution would be dependent on the intermolecular cohesive force existing in the medium and this characterises as well the viscosity of the medium. Thus some sort of interdependence was expected by us between the compressibility and the viscosity of the solution. In the case of electrolytic solutions it is well known that with most electrolytes the relative viscosity of the solution (compared to water) increases with concentration, and the viscosity is always greater than that of the solvent, whereas in the case of some electrolytes, specially, with the heavy-molecule alkali halides, the relative viscosity at first decreases and then increases with concentration and the viscosity of the solution is very often lower than the viscosity of water. It was, therefore, expected that although the compressibility of most of the electrolytes decreases with concentration, *i.e.*, the velocity increases with concentration, some heavy alkali halide solution might show a decrease of velocity with concentration and thus perhaps an increase of compressibility with concentration. It should be noted in this connection that the variation of density with concentration is quite regular without having any maximum or minimum for all the electrolytes. Hence the shape of the compressibility curves is determined primarily by the shape of the velocity curves. With this view we have measured the velocity of supersonic waves in some electrolytic solutions which show abnormal

viscosity and have taken our measurements at different temperatures. It will be evident from the graphs of relative velocity against concentration, that these solutions show abnormal behaviour with regard to the velocity as well, although under not exactly the same condition of temperature and concentration.

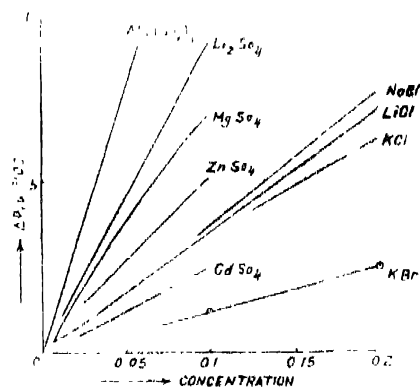


FIG. 1

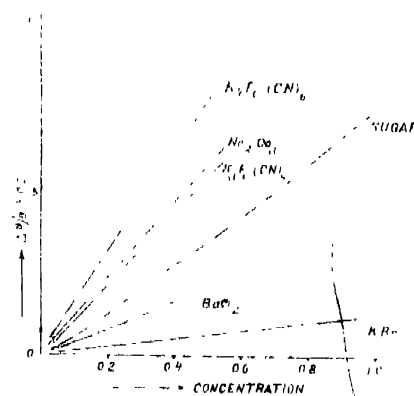


FIG. 1a

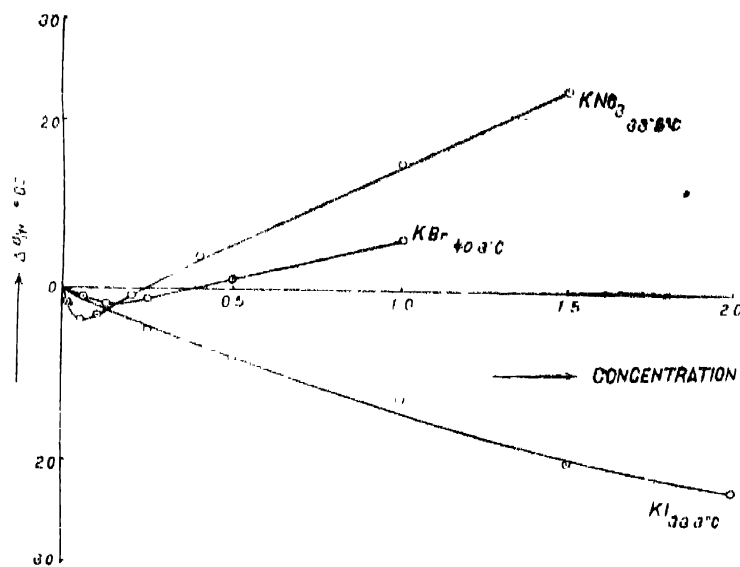


FIG. 2

Figs. 1 and 1a show the relative velocity of supersonic waves in electrolytes as obtained by Szalay and by Falkenhagen and Bachem. In Fig. 2 the relative velocity of supersonic waves in particular electrolytes selected by us for their abnormal viscosity curve have been plotted. They show a decrease of velocity with concentration at the lower concentration ranges and then an increase of velocity. In all other electrolytes so far studied by other workers this peculiarity has not been noted. Further, the course of the velocity-concentration graph changes appreciably at different temperatures. The decrease of relative velocity with concentration, which may be considered as abnormal, is enhanced at higher temperatures. These are shown in

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graphs 3, 3a, 3b. It will be seen, for example, with KI at higher temperatures, that the compressibility is very much increased compared to that of

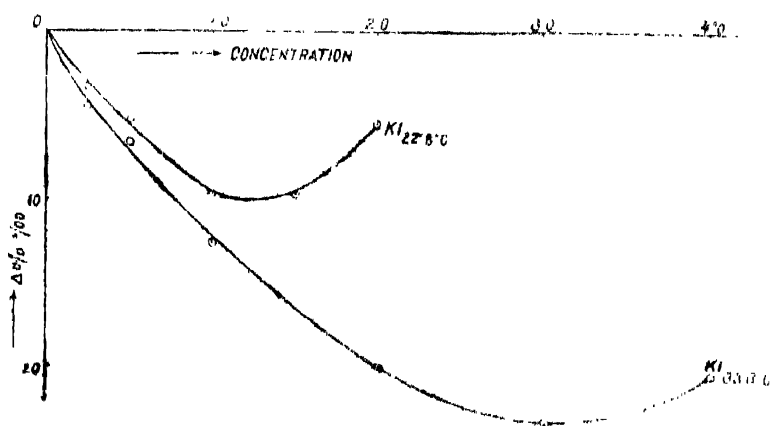


FIG. 3

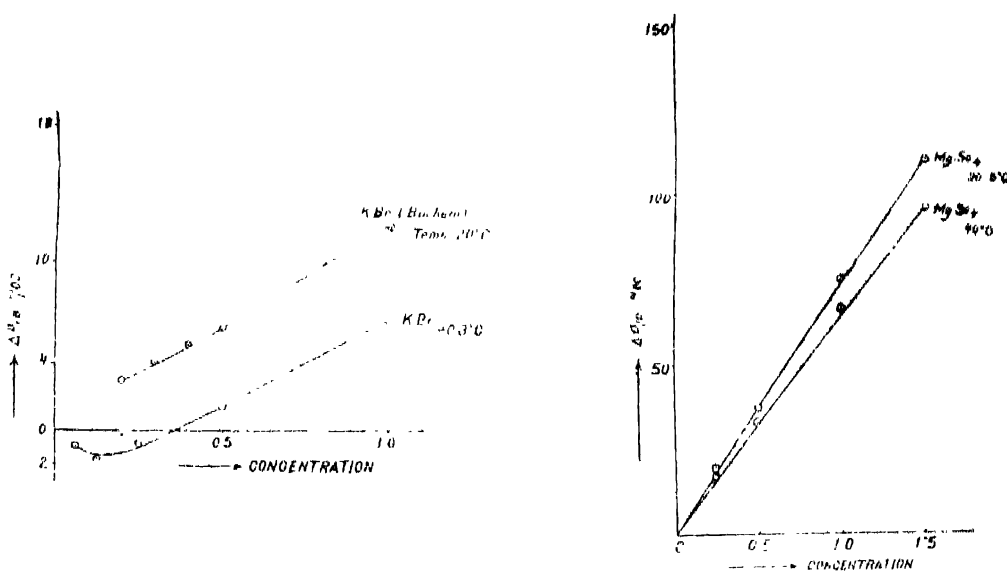


FIG. 3a

FIG. 3b

water. Our ideas up to the present were that the compressibility always decreases when an electrolyte is dissolved in water. The finding is thus corroboratory to the idea obtained from the study of relative viscosity-concentration curves that electrolytes fall into two distinct groups according as they increase or tend to decrease the viscosity of water when dissolved. The variation with temperature of the relative viscosity-concentration curves are drawn in Fig. 4, for comparison, from which it will be apparent that there is a peculiar difference in the two classes of electrolytes both from the standpoint of viscosity and the velocity of elastic waves. Other workers have so far failed to note this peculiarity.

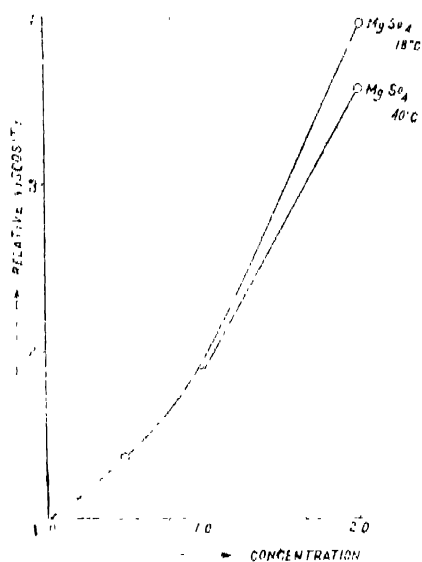


FIG. 4

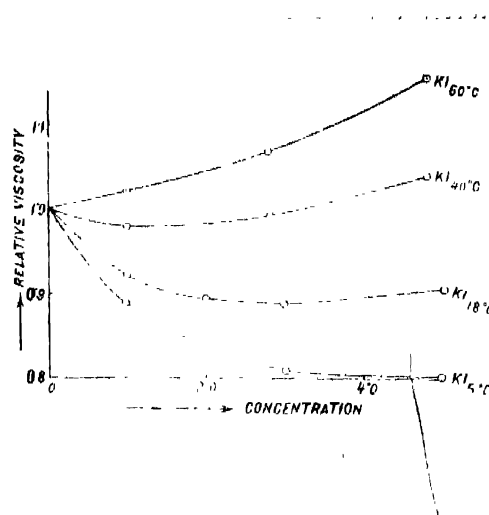


FIG. 4a

It is interesting to note that at a higher temperature the percentage-variation of velocity of both KI and MgSO<sub>4</sub>, the two typical cases, decreases. This indicates a decrease of cohesive force between the components of the solution at a higher temperature and one would expect a decrease of relative viscosity as well with the rise of temperature. But whereas MgSO<sub>4</sub> shows the decrease in relative viscosity, KI shows an increase of relative viscosity with the rise of temperature. Since this increase of viscosity in the case of KI is not due to the increase of cohesive force between the components as proved by a decrease of relative velocity, *i.e.*, an increase of relative compressibility with temperature, one is almost forced to the conclusion that with KI type of molecules, the dimension of each moving component increases with temp., *i.e.*, the KI molecules attach more water molecules around the ions as the temperature increases. This becomes plausible in view of the fact that at the higher temperature, the association in water breaks up more easily or is already broken up and thus water molecule can be attached to the KI ions in solution. The idea of attachment of water molecules to heavy alkali halide ions was also suggested by Prins<sup>7</sup> when working on X-rays of electrolytic solutions. The idea fits in with the finding that the compressibility in KI is greater than that of pure water as against the general behaviour of other group of electrolytes and further that the increase of compressibility is more pronounced the higher the temperature.

The relationships brought forth in the above work call for a diversion of procedure in tackling with the compressibility of electrolytic solutions. So far, attempts have been made to look into the compressibility data from the ionic standpoint. But our work reveals that compressibility of electrolytic solutions might be better understood if we look into it from an angle from which viscosity of the solution might as well be viewed. This requires

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a better understanding of the phenomenon of viscosity of solutions. Attempts are being carried out in this direction.

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