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A Method for the Determination of the Mass of Electrolytic Ions

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I.

THE question how many molecules of a solvent are intimately connected with the different ions in a solution is far from being solved. It occurred to me that we could perform some improvement if a method could be found enabling us to determine directly the masses of ions. Ordinarily the mass does not enter at all in our considerations and the reason is that the forces due to the friction of the ions in the solvent are so much larger than the dynamical reactions due to the masses. For an ion moving with a velocity v in a liquid, the frictional force may be put equal to ρv and the factor ρ is (for water as a solvent) of the order of magnitude $2 \cdot 10^{-9}$, as the friction is comparable to that of a sphere of radius 10^{-8} cm, according to Stokes' formula. On the other hand, the dynamical reaction due to acceleration is $m(dv/dt)$ if m is the mass of the ion. If therefore we consider an ion in a field of high frequency ω (number of vibrations in 2π sec.) the dynamical coefficient to be compared with ρ is ωm . In order to make this coefficient equal to ρ for an ion of the mass of an hydrogen atom ($1.64 \cdot 10^{-24}$ g), the frequency would have to be equal to approximately $\omega = 10^{15}$ and for a mass a hundred times larger, we would still find $\omega = 10^{13}$. This means that mass effects such as we are considering here would not become important in comparison with friction effects except in the infrared region. However, in this region considering ordinary solutions in water as an example, it is doubtful if measurements of the absorption coefficient of infrared waves would give much information, as the proper absorption of the water itself will be important. That is why I tried to look for an effect, which is zero as long as the dynamical reactions of the ions are neglected and would therefore provide us with a direct measurement of these reactions alone. Suppose we introduce supersonic waves in a solution of an electrolyte. If then only frictional forces should exist between the ions and the

solvent, there will be no difference between the velocity of the ions and the velocity of the surrounding liquid. The solution will behave like a homogeneous liquid. If, however, the dynamical reactions are taken in account, these reactions will be different for ions of different masses. As a result, the motion, say of the positive ions, may differ from that of the negative ions. But this means that periodically changing electric charge densities will accompany the sound waves. That is why we should expect potential differences of the period of the sound waves set up between different points of an electrolyte solution by the passing of sound waves. It is obvious that if we can detect and measure this effect, we will be able to draw definite conclusions as to the masses of the ions and in this way as to the number of solvent molecules connected with them.

II.

It remains first of all to be seen what the magnitude of the presumed effect will be. For this purpose the following calculation is presented. No account is taken of interionic attraction, but I think that we may safely wait for the experiments to be performed first as no fundamental change in the results is to be expected from this improvement, although the absolute value of the effect will be influenced especially for higher concentrations.

Suppose the solution contains per cc: $n_1, n_2, \dots n_i, \dots$ ions of charges $e_1, e_2, \dots e_i, \dots$ with the friction constants $\rho_1, \rho_2, \dots \rho_i, \dots$ and the masses $m_1, m_2, \dots m_i, \dots$. If at a certain moment, t , and in a certain place, which we will characterize by one single variable, x (only considering plane waves going in the direction x), the velocity of the solvent is v_0 and the velocity of the ions are $v_1, v_2, \dots v_i, \dots$ we have a first set of equations of the form

$$e_i X - \rho_i(v_i - v_0) = m_i(dv_i/dt). \quad (1)$$

They are equal in number with the number of

different ions contained in the solution and express that in every moment the total force acting on one ion has to be equal to its mass times its acceleration. The force on the left-hand side of (1) is made up of two parts, one part $e_i X$ due to the electric component X of the forces, which in turn will be due to the electric charges in the solution, provided such charges appear. The other part, $-\rho_i(v_i - v_0)$ is the frictional force, which will result as soon as there is a difference between the actual velocities of the ion and the surrounding liquid.

A second set of as many equations as the number of different ions present is furnished by the equations of continuity, expressing that the gain in number of ions contained in an element of volume can only be due to ions entering or leaving through its surface.¹

$$\frac{\partial n_i}{\partial t} + \frac{\partial}{\partial x}(n_i v_i) = 0. \quad (2)$$

Calling the number of different ions z , we have now $2z$ equations for $(2z+1)$ variables, namely z numbers $n_1, n_2, \dots, n_i, \dots$; z velocities $v_1, v_2, \dots, v_i, \dots$, and one additional variable, the field strength X . We make up for this deficiency in adding Poisson's equation, which has the form

$$D \frac{\partial X}{\partial x} = 4\pi \sum_i n_i e_i \quad (3)$$

if D is the dielectric constant of the solvent.

III.

In order to solve these equations for the case in consideration, we assume

$$v_0 = a_0 e^{i(\omega t - kx)}. \quad (4)$$

If g is the velocity of the sound waves, we have

$$k = \omega/g = 2\pi/\Lambda \quad (4a)$$

denoting with Λ the wave-length of the sound waves in the liquid.

The number of ions per cc n_i , will always be very nearly equal to its equilibrium value \bar{n}_i . We put

$$n_i = \bar{n}_i + \nu_i \quad (5)$$

¹ Diffusion is not considered; its effect is altogether negligible for our problem.

and try the assumption

$$\nu_i = \alpha_i e^{i(\omega t - kx)} \quad (5a)$$

with the unknown values of the α_i .

At the same time we assume

$$X = A e^{i(\omega t - kx)} \quad (6)$$

with a value of A which is also unknown and has to be determined.

Considering the two facts that ν_i is very small compared with \bar{n}_i and that $\sum \bar{n}_i e_i = 0$, our equations take the form

$$\begin{cases} e_i X - \rho_i(v_i - v_0) = m_i(\partial v_i / \partial t). \\ \partial \nu_i / \partial t + \bar{n}_i(\partial v_i / \partial x) = 0. \\ D(\partial X / \partial x) = 4\pi \sum_j \nu_j e_j. \end{cases} \quad (7)$$

Here moreover $\partial v_i / \partial t$ has been written instead of dv_i/dt , which is admissible as long as the velocities can be considered as small.

By introducing our special assumptions about the disturbance as due to a sound wave, the Eqs. (7) become

$$\begin{cases} e_i A - \rho_i(a_i - a_0) = i\omega m_i a_i \\ i\omega \alpha_i - ik\bar{n}_i a_i = 0 \\ -ikDA = 4\pi \sum_j e_j \alpha_j \end{cases} \quad (8)$$

Combining the last equations of (8), we find

$$A = i(4\pi/D\omega) \sum_j \bar{n}_j e_j a_j \quad (9)$$

and introducing this value of A into the equations of the first row, the result is

$$(\rho_i + i\omega m_i)a_i - i \frac{4\pi e_i}{D\omega} \sum_j \bar{n}_j e_j a_j = \rho_i a_0 \quad (10)$$

representing z equations to determine the z values of $a_1, a_2, \dots, a_i, \dots$ as multiples of the value a_0 characteristic for the velocity of the solvent.

For all practical purposes it will be enough to give an approximate solution of these equations, keeping in mind that always ωm_i will be very small compared with ρ_i .

A zero order solution will be attained if we neglect ωm next to ρ altogether. Multiply every one of the Eqs. (10) with the corresponding product $\bar{n}_i \cdot e_i / \rho_i$ and take the sum of all the equations. The result will be

$$\sum_j \bar{n}_j e_j a_j \left[1 - i \frac{4\pi}{D\omega} \sum_i \frac{\bar{n}_i e_i^2}{\rho_i} \right] = a_0 \sum_i n_i e_i = 0,$$

showing that in a zero order approximation $\Sigma_j \bar{n}_j e_j a_j = 0$, which according to (9) would mean $A=0$ and therefore no potential differences at all. If they occur nevertheless we see that they will be exclusively due to the dynamical reactions of the ions measured by the products ωm_i . Now if as we found in the zero order approximation $A=0$, and if ωm is neglected, the first row of (8) shows that in this approximation $a_i = a_0$. In a next *first* order approximation we will assume

$$a_i = a_0 + \beta_i \quad (11)$$

and treat β_i as a small quantity, neglecting products of β_i with the small quantities $\omega m_i / \rho_i$. Divide every equation of (10) by the corresponding value of ρ_i and keep in mind the rule of the first order approximation. Instead of the Eqs. (10) we will then arrive at the equations

$$\beta_i - i \frac{4\pi}{D\omega} \frac{e_i}{\rho_i} \sum_j n_j e_j \beta_j = -i \frac{\omega m_i}{\rho_i} a_0. \quad (12)$$

This set of equations enables us at once to calculate the value of $\Sigma \bar{n}_j e_j \beta_j$; we find

$$\begin{aligned} \Sigma \bar{n}_j e_j \beta_j [1 - i(4\pi/D\omega) \Sigma (\bar{n}_j e_j^2 / \rho_j)] \\ = -i\omega \Sigma (\bar{n}_j e_j m_j / \rho_j) a_0. \end{aligned} \quad (13)$$

Now according to (9) and (11),

$$A = i(4\pi/D\omega) \Sigma \bar{n}_j e_j a_j = i(4\pi/D\omega) \Sigma \bar{n}_j e_j \beta_j. \quad (13a)$$

In this approximation we will have an electric field and the field strength will be determined by the expression for A , which results from the combination of (13) and (13a), namely

$$\frac{A}{a_0} = \frac{4\pi}{D} \frac{\Sigma (\bar{n}_j e_j m_j / \rho_j)}{1 - i(4\pi/D\omega) \Sigma (\bar{n}_j e_j^2 / \rho_j)}. \quad (14)$$

The field strength X itself is according to (6) represented by

$$X = A e^{i(\omega t - kx)}.$$

IV.

To discuss the magnitude of the effect we go back to the potential Φ of which the field strength X can be deduced by the well-known equation $X = -\partial\Phi/\partial x$. For this potential, the expression

$$\Phi = ga_0 \frac{(4\pi/D\omega) \Sigma (\bar{n}_j e_j m_j / \rho_j)}{i + (4\pi/D\omega) \Sigma (\bar{n}_j e_j^2 / \rho_j)} e^{i(\omega t - kx)} \quad (15)$$

is easily found starting with the value for A indicated in (14). So we get the result that a sound wave travelling with the velocity g and in which the velocity of the medium oscillates between $\pm a_0$ will be accompanied by a potential wave travelling with the same velocity and in which the potential will oscillate between the values of $\pm \Phi_0$, this amplitude being represented by the formula

$$\Phi_0 = ga_0 \frac{(4\pi/D\omega) \Sigma (\bar{n}_j e_j m_j / \rho_j)}{[1 + (4\pi/D\omega) \Sigma (\bar{n}_j e_j^2 / \rho_j)]^{1/2}}. \quad (16)$$

At the same time the material wave and the potential wave will show a phase difference which, however, we need not consider here.

We observe that the expression $\Sigma (\bar{n}_j e_j^2 / \rho_j)$ is nothing else than the conductivity of the solution expressed in electrostatic units, which we will denote by l . Introducing this notation a more convenient form for Φ_0 will be

$$\Phi_0 = ga_0 \frac{\Sigma (\bar{n}_j e_j m_j / \rho_j)}{\Sigma (\bar{n}_j e_j^2 / \rho_j)} \frac{4\pi l / D\omega}{[1 + (4\pi l / D\omega)^2]^{1/2}}. \quad (16a)$$

If now we have a solution of one salt containing \bar{n} molecules per cc, of which every one is split in $p_1, p_2, \dots, p_i, \dots$ different ions of valencies $\zeta_1, \zeta_2, \dots, \zeta_i$, we have $\bar{n}_j = p_j \bar{n}$; $e_j = \zeta_j e$, where e is the electronic charge ($4.77 \cdot 10^{-10}$ e.s.u.) and the valency ζ_j is taken with its appropriate sign; $m_j = M_j m_H$, if M_j is the molecular weight of the ion, together with the bound solvent molecules and m_H is the mass of the hydrogen atom $1.64 \cdot 10^{-24}$ g. Introducing these notations we find

$$\Phi_0 = \frac{m_H}{e} ga_0 \frac{\Sigma (p_i \zeta_i M_i / \rho_i)}{\Sigma (p_i \zeta_i^2 / \rho_i)} \frac{4\pi l / D\omega}{[1 + (4\pi l / D\omega)^2]^{1/2}}. \quad (16b)$$

Now, if as an example we are dealing with a 10^{-3} normal solution of a binary salt like KCl or LiBr, etc., the order of magnitude of l will be $l = 10^9$ (if we assume $\rho = 2 \cdot 10^{-9}$) and therefore assuming $D = 80$ the quotient $4\pi l / D\omega$ will become equal to 1 for $\omega = 10^8$ approximately. This frequency would roughly correspond to radio waves of 30 meters wave-length and would make the last part of the expression (16b) equal to $2^{-1/2}$. Using a lower frequency (for the special solution considered) would mean bringing the value of that part of the expression nearer to 1. The same thing would occur if the concentration is increased. That is

why in judging the magnitude of the effect we will take it that the expression $(4\pi l/D\omega)/[1+(4\pi l/D\omega)^2]^{1/2}$ can and has been made equal to 1. By adopting the usual values for m_H and ϵ and taking $g=1.4 \cdot 10^5$ cm/sec., the first factor in (16b) becomes equal to $(m_H/\epsilon)ga_0=4.8 \times 10^{-10}a_0$. By using this factor the potential would be expressed in electrostatic units. Using volts instead, we find for the order of magnitude of Φ_0 , the value

$$\Phi_0 = 1.4 \times 10^{-7} a_0 \frac{\sum (p_i \zeta_i M_i / \rho_i)}{\sum (p_i \zeta_i^2 / \rho_i)} \text{ volts.} \quad (17)$$

Now in our example, we would have $p_1=p_2=1$, $\zeta_1=+1$, $\zeta_2=-1$ and therefore instead of (17)

$$\Phi_0 = 1.4 \times 10^{-7} a_0 \frac{M_1/\rho_1 - M_2/\rho_2}{1/\rho_1 + 1/\rho_2} \text{ volts.} \quad (17a)$$

It is obvious that with $a_0=1$ cm/sec. and with appropriate salts, the oscillations of the potential

should attain values of some 10^{-6} volts, which can easily be detected by ordinary amplification methods.

The question if $a_0=1$ cm/sec. is not too large a value to be assumed, remains to be answered. Now this velocity amplitude corresponds to a pressure-amplitude of $1/7$ atmosphere and to an energy delivered per cm^2 and sec. of $1/200$ Joule. It seems that this is not unreasonable at all thinking of a vibrating quartz-crystal, and that even more can be expected.

Experiments to detect the effect discussed here are being set up; no definite results are as yet available. As, however, the considerations put forward in this article seem to lead to an entirely new attack on the problem of solvation, I hope that I may be permitted to present them even in their present incomplete form in order to share in the congratulations at the birthday of this new journal.