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A NOTE ON THE MAGNETIC SUSCEPTIBILITY OF SOLUTIONS

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ABSTRACT

It is shown that, when a solution of ions of different magnetic susceptibilities is placed in a magnetic field, there is a difference between the concentrations of the solute in the field and outside of the field. This difference, however, is so small that it can hardly be measured experimentally; therefore, it cannot vitiate the measurements of the magnetic susceptibility of solutions by the classical methods.

WHEN a particle of magnetic moment μ is placed in a non-homogeneous magnetic field of intensity $H(x)$, this particle experiences a force given by $\mu\ dH/dx$. All atoms or ions possess a magnetic moment in a magnetic field. This moment is either permanent (paramagnetism) or induced by the field following the Larmor rotation (diamagnetism). Thus, when a non-homogeneous field is applied to a solution, the ions will be subjected to a force of attraction or repulsion, depending on their para- or diamagnetism and which varies with their susceptibilities. The motion of the ions, would, in general, produce a different concentration of positive and negative charges, but the electric field intensity dv/dx where V is given by $\triangle \mathrm{v} = -4\pi\rho$, ρ being the density of electricity, would be so great compared to the magnetic force or the diffusion, that we will assume the solution to be electrically neutral at every point. When a gradient of concentration is established, the ions will tend to diffuse back and an equilibrium will be reached. It is the conditions of this equilibrium we wish to investigate.

2. Let us suppose that we have a cylindrical container of cross section q, the x axis of our coordinates corresponding to the axis of the container. A magnetic field of intensity $H(x)$ is placed along the x axis, $H(x)$ increasing with x and such that $H(0)=0$.

We have dissolved $N_1\ N_2 \cdots N_i \cdots N_s$ ions of charge $z_1\epsilon,\ z_2\epsilon \cdots z_i\epsilon \cdots z_s$. in the volume V; as the solution is electrically neutral

$$\sum_{i=1}^{s} N_i z_i = 0.$$

The ionic concentrations or the number of ions per unit volume will be denoted by $n_1, n_2, \cdots, n_i, \cdots, n_s$. An ion i has an average magnetic moment in the direction of the field given by

$$\mu_i = \sigma_i H$$

where $\sigma_i = \mathrm{X}_m/N$ if X_m is the molecular susceptibility of the ion and N Avogadro's number, for the diamagnetic moment is proportional to the field inducing it, and the paramagnetic average moment is due to the orientation by the field of the permanent moment.

Let us now calculate the forces acting on an ion. The magnetic force is $\mu_i(dH/dx)=\sigma_i H(dH/dx)$. The electric force is $z_i\epsilon(dV/dx)$ where dV/dx is the field intensity producted by the distribution of the ions of different signs.

The force due to the diffusion is easily obtained if we consider that the osmotic pressure is responsible for this force.[1]

If we take a slice of thickness dx of the solution, on one side there is a concentration $n_i(x)$ of the ions of type i, on the other side $n_i(x+dx)$. The osmotic pressure due to the i ions will then be $p_i(x)$ and $p_i(x+dx)$ so that the total resultant force acting on the volume qdx is

$$-(dp_i/dx)qdx$$

and the force per ion will be

$$-dp_i/ndx$$

as there are $n_i qdx$ ions in the volume qdx.

We shall now assume that the solution follows van t'Hoff Law of osmotic pressure. It will be shown further that for strong electrolytes, for which van t'Hoff Law does not hold, we have to introduce a correction factor which does not greatly modify our conclusions. Then $p_i=n_ikT$ (T absolute temperature, k Boltzmann's constant), and

$$-dp_i/n_idx=-kTdn_i/n_idx$$

When the equilibrium is reached the sum of the forces acting upon the ion must equal zero.

$$-kTdn_i/n_idx+z_iedV/dx+\sigma_iHdH/dx=0 \quad (i=1,2,\cdots,i\cdots s) \tag{1}$$

Between any two equations (1) we can eliminate dV/dx which gives us

$$-kT\left(\frac{z_i}{n_j}\frac{dn_j}{dx}-\frac{z_j}{n_i}\frac{dn_i}{dx}\right)+H\frac{dH}{dx}(\sigma_jz_i-\sigma_iz_j)=0$$
$$(j=1,2,\cdots,i-1,\ i+1,\cdots,s)$$

or integrating

$$kT\log\left(\frac{n_j}{n_j^0}\right)^{z_i}\left(\frac{n_i^0}{n_i}\right)^{z_j}=\frac{H^2}{2}(\sigma_jz_i-\sigma_iz_j)$$

where the n^0's are the concentrations at $H=0$ or $x=0$. Solving for n_j we have

$$n_j=n_j^0(n_i/n_i^0)^{z_j/z_i}e^{H^2(\sigma_jz_i-\sigma_iz_j)/2kTz_i} \quad (j=1,2,\cdots,i-1,i+1,\cdots,s) \tag{2}$$

Now to adjust n_i so as to satisfy the condition of electrical neutrality at every point

$$\sum_{j=1}^{s}n_jz_j=0 \tag{3}$$

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[1] Nernst, Zeits. f. Phys. Chemie **2**, 613 (1888).

Replacing (2) in (3)

$$n_i z_i + \sum_j{}' z_j n_j{}^0 (n_i/n_j{}^0)^{z_j/z_i} e^{H^2(\sigma_j z_i - \sigma_i z_j)/2kTz_i} = 0 \tag{4}$$

The accent on the summation meaning that we must omit the term $j=i$ in the addition. As $n_i/n_i{}^0$ is very nearly unity we can write

$$(n_i/n_j{}^0)^{z_j/z_i} = 1 + (z_j/z_i)(n_i/n_i{}^0 - 1) + \cdots$$

and (4) becomes

$$n_i z_i + \sum_j{}' z_j n_j{}^0 e^{H^2(\sigma_j z_i - \sigma_i z_j)/2kTz_i}\left(1 - \frac{z_j}{z_i}\right) + \frac{n_i}{n_i{}^0} \sum_j{}' \frac{z_j{}^2}{z_i} n_j{}^0 e^{H^2(\sigma_j z_i - \sigma_i z_j)/2kTz_i} = 0$$

or

$$\frac{n_i}{n_i{}^0} = \frac{\sum_j z_j n_j{}^0 e^{H^2(\sigma_j z_i - \sigma_i z_j)/2kTz_i}(z_j - z_i)}{\sum_j z_j{}^2 n_i{}^0 e^{H^2(\sigma_j z_i - \sigma_i z_j)/2kTz_i}} \tag{6}$$

For the other ions we would have

$$\frac{n_j}{n_j{}^0} = \left[\frac{\sum_j z_j n_j{}^0 e^{H2(\sigma_j z_i - \sigma_i z_j)/2\,kTz_i}(z_j - z_i)}{\sum_j z_j{}^2 n_j{}^0 e^{H^2(\sigma_j z_i - \sigma_i z_j)/2\,kTz_i}}\right]^{z_j/z_i} e^{H^2(\sigma_j z_i - \sigma_i z_j)/2\,kTz_i}$$

The n^0's would have to be determined from the equations $\int n_i dx = N_i$. The solution of our problem is then given by (6) and (7).

3. *Application to N_iSO_4.* This salt is dissociated into two ions Ni^{++} and SO_4^{--}. Thus $s=2$ and $z_1 = -z_2$. The molecular susceptibilities are for *Ni*, $\chi_m = 1.5\ 10^{-3}$ cm/mole and for SO_4, $\chi_m = -3.8\ 10^{-5}$ cm/mole. This gives $\sigma_1 = 2.5\ 10^{-27}$ cm and $\sigma_2 = -6.3\ 10^{-29}$ cm. We will assume $T = 300°K$ and $H = 10{,}000$ gausses.

Equation (3) becomes

$$2n_1 - 2n_2 = 0 \qquad n_1 = n_2 = n$$

and

$$2n_1{}^0 - 2n_2{}^0 = 0 \qquad n_1{}^0 = n_2{}^0 = n^0$$

Equation (6) finally gives

$$n/n^0 = 1.0000015$$

This small value of the difference in concentrations in the field and outside, is almost impossible to detect, at least it cannot change anything in the results of the measurements of the magnetic susceptibility of solutions. The equations (6) and (7) can also be applied to a mixture of solutions but in this case again it is easy to see that $n_i/n_i{}^0$ is going to be of the same order of magnitude as above. The theory could also be easily extended to a mixture of liquids. In this case the result is simply

$$n/n^0 = e^{\sigma H^2/2kT}$$

That is to say n/n^0 is again of the same order of magnitude.

4. If instead of van t'Hoff formula for the osmotic pressure we use the value given by the Debye and Huckel's theory,[2] we shall have to modify our equations somewhat.

$$p_k = \sum_i \left[n_i kT - (e^2\kappa/6D) n_i z_i^2 \eta_i\right]$$

where D is the dielectric constant of the solvent, $\kappa^2 = (4\pi\epsilon^2/DkT)\sum_j n_j z_j^2$ and η_i is a function of $u_i = \kappa a_i$ where a_i is the diameter of the ion.

$$\eta_i = (3/u_i^3 [(1+u_i) - 2\log(1+u_i) - 1/(1+u_i)]$$

If we follow the same procedure as before we get a very complicated expression which for a solution containing two types of ions only reduces to (supposing n_1/n_1^0 almost equal to one)

$$n_1 - n_1^0 = [(z_2\sigma_1 - z_1\sigma_2)H^2/2]/(kT/n_1^0)(z_1 - z_2) + (\epsilon^2 \xi z_1 z_2/6D)\{\xi[a_1(1+2z_1) - a_2(1+2z_2)] + (1/2(n_1^0)^{1/2})(z_2 - z_1)(1 + z_1 z_2)\}$$

where

$$\xi = [(4\pi\epsilon^2/DkT)(z_1^2 - z_1 z)_2]^{1/2}$$

This is again a value of the same order of magnitude as that derived from van t'Hoff equation.

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[2] Debye and Huckel, Phys. Zeit. **24,** 185 (1923).