Hall voltage in electrolyte solutions

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Abstract—Hall coefficient for $CuSO_4$ liquid electrolyte has been measured and found to be positive. Detection of Hall signal was limited to dc methods although ac techniques were also investigated. The Hall coefficient increases with decreasing concentration of solute and for distilled water approaches 5×10^5 cm³/coul. Calculations of H^+ ion mobility using the two carrier expression for Hall coefficient show the charge carrier in a liquid electrolyte to be the H^+ ion. Mobility of the proton in water is of the order of 1 cm² volt-sec, which is near the value in ice.

1. Introduction

Hall effect in a liquid electrolyte was first studied experimentally in 1882 by Roiti,[1] who obtained spurious results which he believed were due to local variations of salt concentration. Bagard's work[2] in 1896 indicated that the Hall effect was very large in electrically conducting liquids. Bagard, and also Roiti, used a capillary electrometer to measure the transverse potential. They found that the effect did not appear instantaneously: rate of growth of voltage was at first large and diminished gradually, its magnitude varying with concentration of solute. Bagard's experiment was repeated by others,[3-6] who failed to verify his findings. The effects Bagard reported were attributed to electrode disintegration, vibrational disturbances, temperature variations, and non-uniformity of magnetic field.

The nature of the Hall effect in liquid electrolytes remained obscure until A. E. Oxley[7] obtained positive results in concentrated solutions of copper sulphate, silver nitrate, cadmium sulphate, and in copper sulphate gels. Although the potentials measured by Oxley were very small in contrast to Bagard's they reversed polarity with

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reversal of current and magnetic field and seemed to confirm the existence of a Hall effect in liquid electrolytes.

More recent investigations have shown that Bagard's claims are verified if a suitable detector is used; i.e., one with a very high input impedance. Using such a detector, Mergault and Pages-Nelson[8] and Laforgue-Kantzer[9] have measured potentials thousands of times greater than expected from calculations of Hall coefficients using standard mobility tables. These measurements were made on concentrated organic and inorganic acid solutions where the proton is believed to be the majority charge carrier. Evseev[10] has observed a large effect in $CuSO_4$ solution. However, his experiment is not sufficiently described to permit quantitative interpretation. The present work was undertaken to study the effect in aqueous salt solutions and to consider using Hall effect measurements to investigate proton mobility in very pure water.

2. Experimental

In our experiments, we investigated both ac and dc methods for measuring the Hall voltage. Techniques for measuring Hall voltage in solids are well known, yet, the unique problems encountered in liquids require a brief description of our experimental procedures.

A. DESIGN OF HALL CHAMBER

The liquid Hall samples in this investigation were similar to those of semiconductors, employing the four probe method. For liquids a rigid cavity must be formed with electrodes suitably placed and sealed to prevent evaporation. The need to disassemble and clean the cell and to vary cell thickness led to the configuration shown in Fig. 1. Parallel slots were cut perpendicular to the long edge of a teflon plate about 4 cm apart to hold the primary electrodes while two smaller slots were cut midway between the two parallel ones on either side of the plate to hold the Hall electrodes. A drop of liquid was placed in the center of the teflon plate and covered by a glass cover plate which distributed the liquid evenly over the cell volume. Electrodes were slipped into the slots and the periphery between the cover plate and teflon base plate sealed with silicone grease. Thickness of the cell was controlled by means of teflon shims of desired
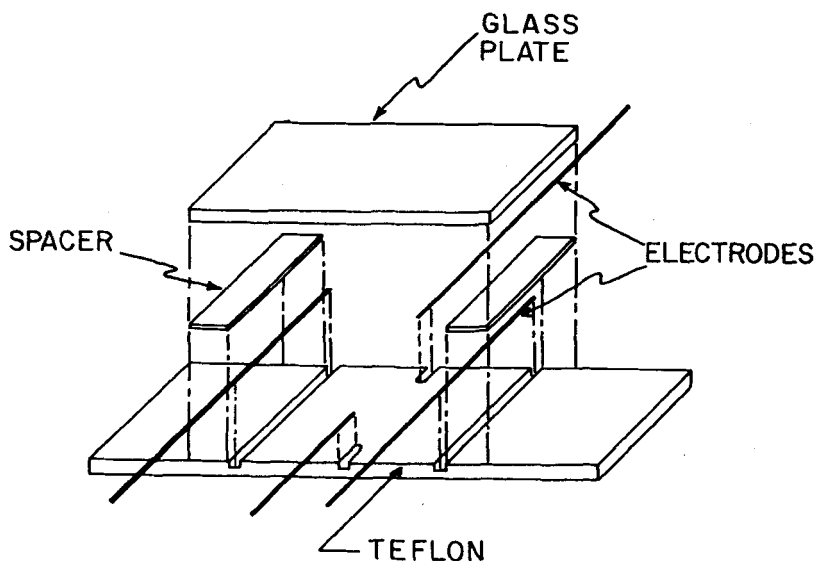
Figure 1. Schematic sketch of exploded Hall cell for liquids. Top glass plate spreads liquid to thickness determined by spacers. Electrodes are removable. Periphery is sealed with silicone grease.

thickness under the edges of the cover plate. Pressure on the glass cover plate (with no shims in place) enabled us to attain liquid films about 15 microns thick. One disadvantage of the film formed in this arrangement was that it did not permit escape of gases, such as hydrogen, produced in electrolysis.

B. DETECTION OF HALL SIGNAL

In high impedance material it is impossible to line up perfectly the two Hall electrodes, hence after the current is turned on a large residual voltage appears. In our ac apparatus the sample was situated in an ac bridge to balance this residual voltage to zero similar to the method of MacDonald and Robinson.[11] The high source impedance of the Hall voltage requires a detector with a very high input impedance. We used a circuit described by Krakauer,[12] which at our highest operating frequency of 1050 Hz, had an input impedance of 10^9 ohms. The output of the detector was amplified for voltage measurement. Overall performance of the detector was tested by measuring the Hall signal of a commercial Hall (InSb)

probe having electron majority charge carrier. The Hall signal of this probe was also used as a standard to determine the sign of the charge carrier in unknown materials by comparison of the respective phases of the Hall signals.

The dc method used a battery for supplying primary current and an electrometer for detecting the Hall emf. A dynamic capacitor type electrometer, having an input impedance of 10^{15} ohms, and voltage sensitivity of 0.2 mv, was found necessary. The residual voltage in this case was reduced by a bucking voltage placed in the Hall circuit. This permitted full utilization of the electrometer sensitivity.

3. Results

Preliminary experiments to detect a Hall signal were made using the ac signal method at various frequencies from 30 to 1050 Hz. Several aqueous electrolyte solutions of NaCl, $CuSO_4$, HCl, and NaOH, in varying concentrations were examined but none yielded a Hall effect.

It was decided to study the dc effect with $CuSO_4$ as electrolyte. This electrolyte was chosen so that gas evolution could be avoided. When the magnetic field was applied, a Hall voltage slowly appeared reaching a maximum in about one or two minutes. Figure 2 shows a typical recorder trace of this effect with the associated decay of the signal after removal of the magnetic field. This signal was also found to reverse polarity with reversal of primary current and magnetic field. Comparison with the standard Hall probe showed the charge carrier in $CuSO_4$ was positive. We tested a variety of materials for the Hall electrodes including, platinum, gold, copper, and nickel chromium alloy, none of which appeared to produce any variation in the signal voltage. As a result we used the nickel chromium alloy for all of our subsequent measurements.

Further verification of a Hall effect was made by changing the current, magnetic induction, and thickness in samples of fixed concentration. The results shown in Figs. 3, 4, and 5, indicate a linear dependence of the Hall voltage on these variables.

The Hall signal could be reduced when a shunt resistance of tens of megohms was connected across the input to the electrometer.
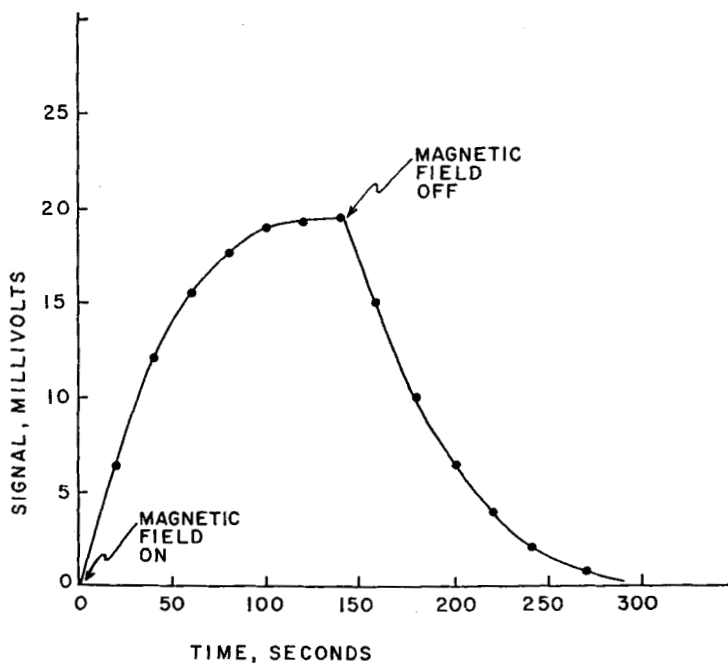
Figure 2. Hall voltage as function of time in 0.01 molar copper sulfate solution in water. Time constant is about 40 secs.
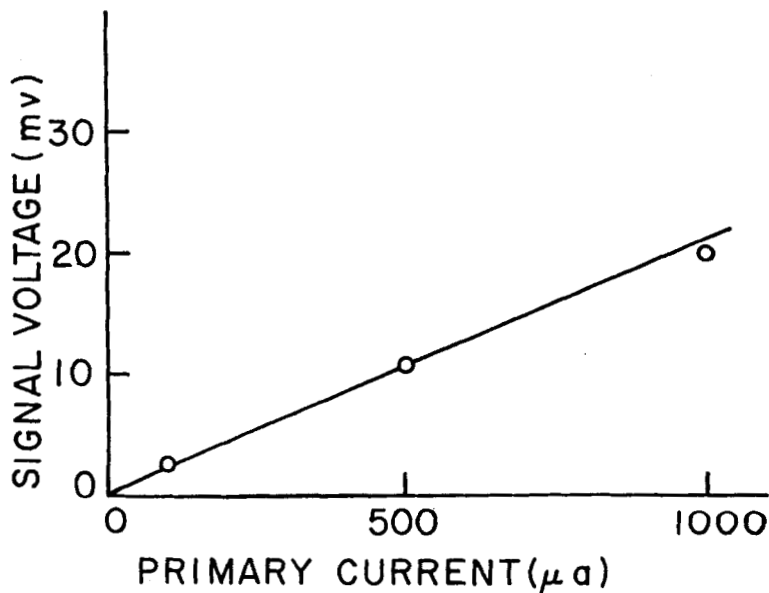

Figure 3. Hall voltage in 0.01 M CuSO₄ in water is a linear function of primary current in the solution.
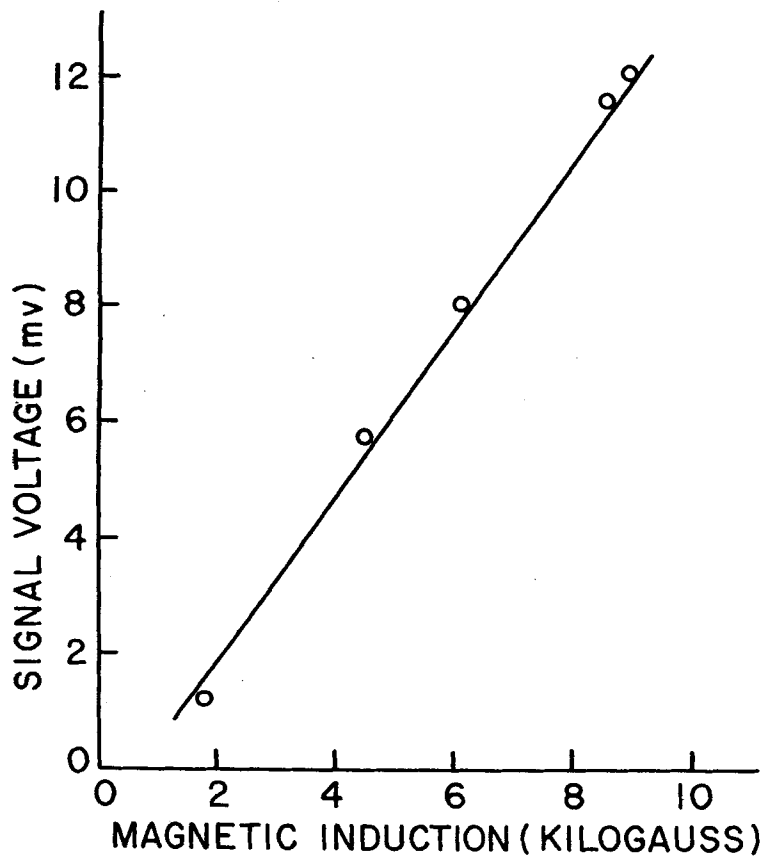
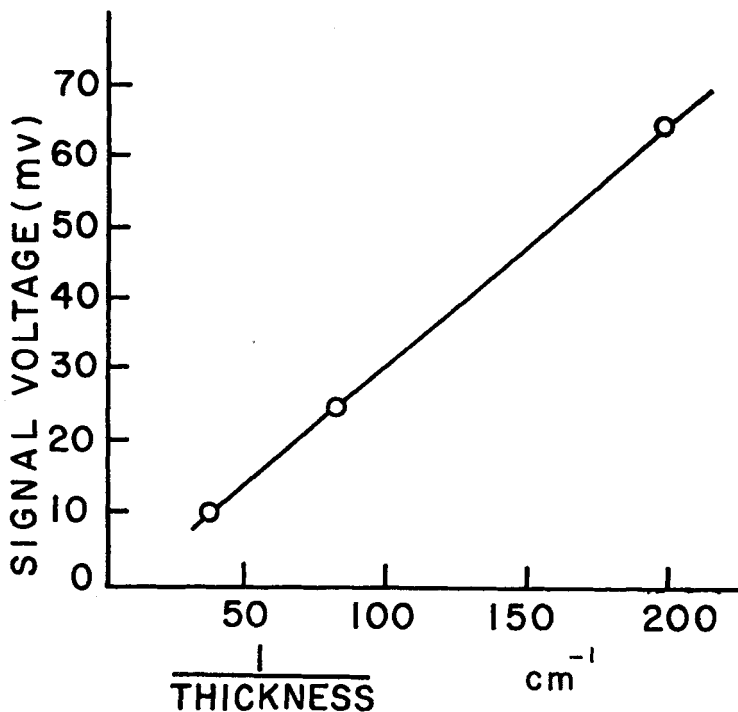Figure 4.   Hall voltage in 0.01 M CuSO₄ in water is a linear function of magnetic field strength.

Figure 5. Hall voltage in 0.01 M CuSO$_4$ in water is a linear function of reciprocal of thickness of conducting solution.

Figure 6 shows this unexpected effect of the shunt resistance.   The reduction in signal means the Hall field is established in a generator having very high internal impedance.   The shape of the curve in Fig. 6 shows the Hall source is shorted out as the shunt resistance is reduced to 1000 megohms.   With a shunt resistance of one megohm,
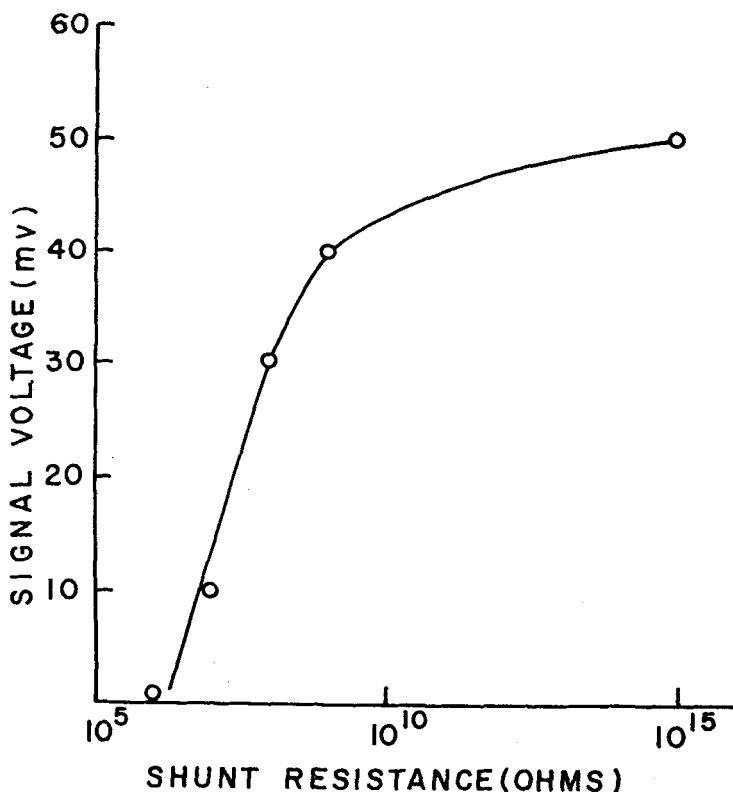
Figure 6.   Effect of shunt resistance across the Hall probes in 0.01 M CuSO$_4$ in water.   Reduction of Hall signal shows the impedance of Hall voltage source to be 100 megohms.

the signal voltage was reduced below the sensitivity of the electrometer.   The available Hall power can be estimated from Fig. 6 by calculating the current through the 100 megohm resistance.   This is approximately 40×10^{-11} amperes, and the corresponding power, 16×10^{-12} watts.

The high impedance of voltage source explains the difficulty encountered by earlier workers in observing the effect. Oxley[7] stated that the resistance of his galvanometer used to measure the Hall current was 16 ohms.

This high impedance may also explain why our ac equipment did not indicate a Hall signal. Although the input impedance of this equipment was about 1000 megohms, as required, according to Fig. 6, the stray impedance to ground of the sample and Hall leads may have been much lower thus shorting out the Hall signal.

In some cases, the Hall signals did not appear uniformly as illustrated in Fig. 2 but made a short initial deflection opposite in polarity to the final equilibrium signal. Also, when the field was removed the signal showed some transient movements before decaying to equilibrium. When this occurred the signal rarely returned to its initial zero value. This may be due to magneto-hydrodynamic phenomena which produce circulation currents in the sample. In thin samples (< 0.5 mm) with good temperature equilibrium these effects were reduced and permitted consistent reproduction of the signal as shown in Fig. 2. Laforgue-Kantzer[9] noted similar effects in his work and shows graphs of the signal behavior.

TABLE 1   Electrical Properties of $CuSO_4$ in Aqueous Solution

c, mole/liter	$\sigma \times 10^3$ in $(\Omega^{-1}\,cm^{-1})$†	$R_H \times 10^{-3}$ cm³/coul	pH‡
1.0	56	0.65	3.5
0.5	35	3.5	3.9
10^{-1}	11	13.3	4.3
0.5×10^{-1}	5.9	60.7	4.7
10^{-2}	1.72	203	5.1
10^{-3}	0.26	272	5.7
H_2O	0.005	500	7.0

† International Critical Tables
‡ Measured at room temperature 25 °C

Table 1 shows the Hall coefficients for several concentrations of $CuSO_4$ obtained from solutions prepared with triply distilled water. Each sample was permitted to stabilize for two hours before a reading

was taken. At high concentration and strong magnetic field, the signals appeared in seconds. In dilute samples, the voltage response rose to a maximum in minutes. In dilute solutions, after the primary current was turned on, the electrometer needle drifted continually in one direction as though the liquid conductivity were changing. This may have been due to increasing temperature from Joule heating or a gradual reduction in electrolyte concentration due to plating out. In many cases the electrometer needle drift could be reversed or accelerated by turning on the magnetic field which seemed to superimpose a Hall voltage on the drift. An average of readings for the two directions of magnetic field was used to cancel out the drift. At high dilutions the results were not accurately reproducible. With triply distilled water a Hall coefficient of about 5×10^5 cm^3/ coul, was tentatively determined.

4. Discussion

When a salt is dissolved in water the increase in conductivity of the solution is due to the resulting dissociated ions. The Hall coefficient for a two carrier system is given by

$$R = \frac{1}{|e|} \cdot \frac{n_+\mu_+{}^2 - n_-\mu_-{}^2}{(n_+\mu_+ + n_-\mu_-)^2} \qquad (1)$$

and if the concentration of carriers are equal we obtain

$$R \simeq \frac{1}{ne} \frac{\mu_+ - \mu_-}{\mu_+ + \mu_-} \qquad (2)$$

The mobility of the copper ion at 25 °C is 4.5×10^{-4} cm^2/volt-sec and for the sulfate ion, it is 7.1×10^{-4} cm^2/volt-sec. Hence, if the electrical conductivity of CuSO$_4$ solutions were due to the dissolved ions, one would expect, from Eq. (2), a negative Hall coefficient. However, our results have shown a positive value for this coefficient over a wide range of solute concentration. This result may be analyzed by considering the dependence of the Hall coefficient on pH and electrical resistivity.

Figures 7 and 8 show log R plotted against the solution pH and log of solution resistivity, respectively, for the solute concentrations shown in Table 1. The curve in each of these figures is made up of two portions that intersect at a concentration of 10^{-2} molar, each
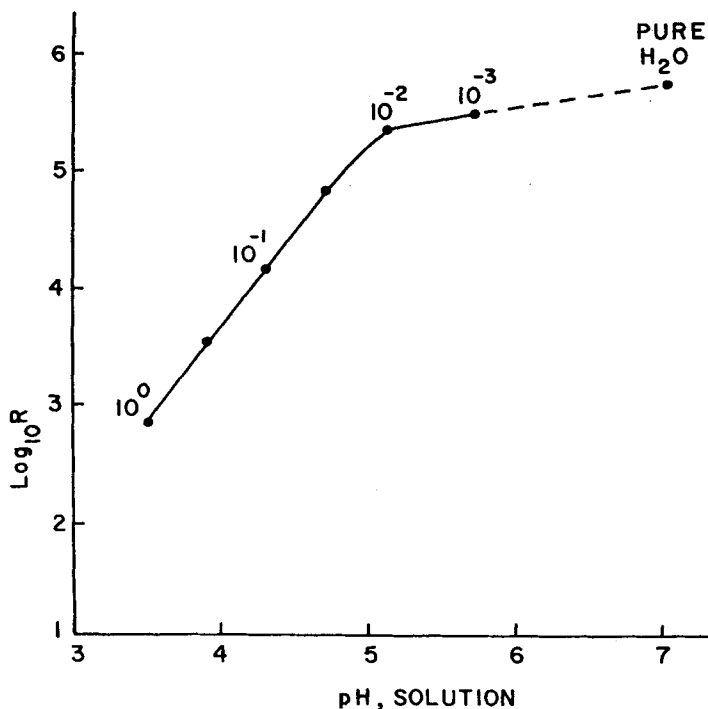
Figure 7. Log of Hall coefficient, R, as function of pH of $CuSO_4$ in water. Figures along curve give molarity of $CuSO_4$.

portion showing a relationship of the form $y = mx + b$. Figure 7 suggests that for $CuSO_4$ solute concentrations greater than 10^{-2} molar, hydrogen ions are responsible for the observed effect, since $ph = -\log n_{H+}$. With n_{H+} expressed as ions/cm³, an equation for this portion of each curve can be obtained. Hence from Fig. 7

$$\log R = -1.66 \log n_{H+} + 31.7 \qquad (3)$$

and from Fig. 8

$$\log R = 1.66 \log \rho + 1 \qquad (4)$$

If the H^+ ion is assumed to be the majority carrier in this region of solute concentration, its mobility can be computed by equating Eqs. (3) and (4), hence: $\log n\rho = 18.5$; and if $\rho = 1/ne\mu$; then, $\mu = 2$ cm²/volt-sec.

The Eqs. (3) and (4) show that $R \sim (1/n)^{3/2}$ and $R \rightarrow (\rho)^{3/2}$ which does not agree with the simple expression for a single charge carrier,
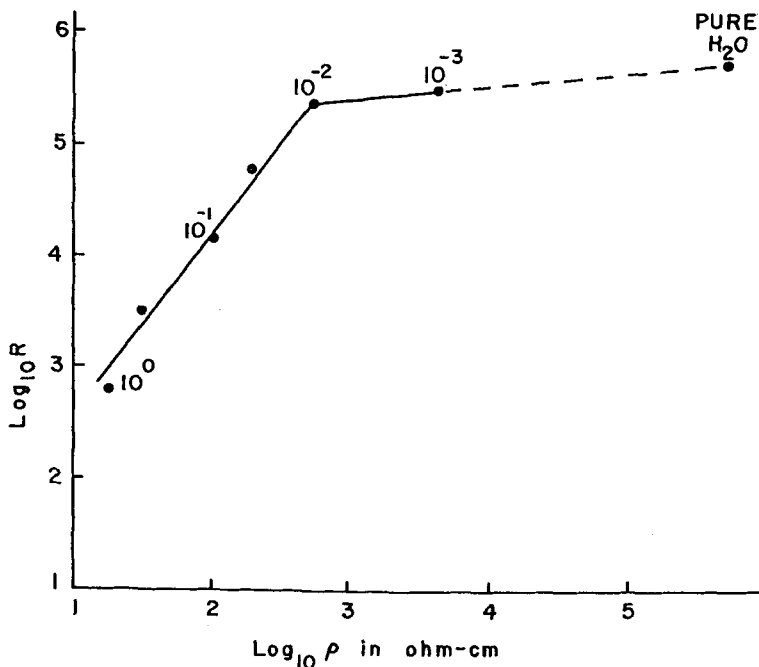
Figure 8. Log of Hall coefficient, R, as function of log of resistivity, ρ, for CuSO$_4$ in water. Figures along curve give molarity of CuSO$_4$.

namely, $R = 1/ne$. It is possible that our Hall coefficient values contain a systematic error that could explain the discrepancy. Since temperature effects could arise from Joule heating the power dissipation in the cell was kept below 0.01 watts. However, the aqueous samples were very thin and it is possible that local heating effects occurred, especially at the electrodes. The mobility determined should however, be independent of systematic error in the Hall coefficient since the slopes of the lines in Figs. 7 and 8 are identical.

The upper portion of the curves in Figs. 7 and 8; corresponding to the more dilute solutions, also show a linear relationship. In this region the hydrogen ion concentration is not predominant. However, the coefficient remains positive for water solutions and up to 10^{-3} molar salt concentration indicating a positive majority charge carrier. At concentrations up to 10^{-3} M CuSO$_4$ the Hall coefficient is indicated by the dashed line as a tentative result. Assuming that Hall

mobilities for water ions can be calculated using Eq. (2) and that the expression for electrical conductivity, $\sigma = ne(\mu_{+} + \mu_{-})$, (where the μ_{+} refers to hydrogen ions, μ_{-} refers to hydroxyl ions and the ion concentrations are equal; i.e., $pH = 7$), by taking $\sigma = 5 \times 10^{6}$ and $R = 5 \times 10^{5}$, we obtain $\mu_{+} = 1.5$ cm²/volt-sec and μ_{-} 1.0 cm²/volt-sec. In this calculation we neglect the influence of dissolved impurities which are undoubtedly present because of the high conductivity of our water compared to conductance water. Nevertheless the hydrogen ion may still predominate over possible impurities as current carriers since mobilities calculated from Hall measurements are determined by the Lorentz force: i.e., they depend on the actual ion velocity. The drift mobility of hydrogen ions in pure water is about 3×10^{-3} cm²/volt-sec at 25 °C, but the actual velocity may be quite different due to the special mechanism of proton transport in water.[13]

A clearer picture of this mobility difference can be made by comparing proton transport in water and ice. The mobility of protons in ice has been shown to be two to three orders of magnitude greater than the drift mobility of hydrogen ions in water. The increased mobility has been interpreted in terms of a change in the rate determining step, namely, from water molecule rotation to proton tunneling between H_3O^{+} and H_2O and between OH^{-} and H_2O.[14,15] Accordingly, the proton mobilities computed above for water would correspond to the mobility within the ice-like aggregates in water where the hydrogen ion is suspected to have a mobility close to that in ice. However, our results are tentative: the Hall coefficient measured in our distilled water may be in error by nearly an order of magnitude.

Similarly, the mobility ($\mu = 2$ cm²/volt-sec) calculated for more concentrated solutions is due to increased ordering of water molecules promoting longer chains of hydrogen bonds as in the formation of ice. The knee of the curves in Figs. 7 and 8 is at about 10^{-2} molar which is the concentration beyond which the Debye-Huckel-Onsager theory becomes invalid. At this concentration the ions of $CuSO_4$ may be relatively stationary compared to the fast moving protons in charge transport.

Summary

The data show the existence of a large Hall effect in aqueous media. For $CuSO_4$ solutions, the coefficient is positive and increases as the concentration approaches that of very pure water. Analysis shows that proton transfer rather than the dissolved solute ion transport is responsible for the electrical conductivity. Hall voltages as large as those reported by others[8,9,10] in the recent literature were not found in this experiment.

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