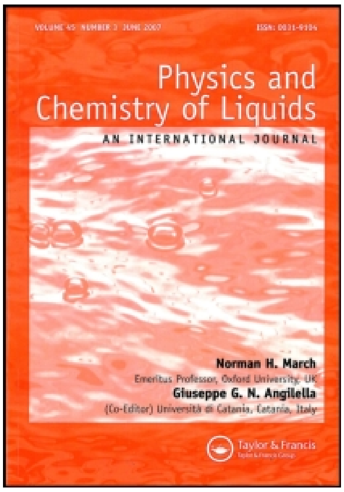

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Plummer, Mitty C. and Ham, Joe S.(1972) 'The hall effect in molten salts', Physics and Chemistry of Liquids, 3: 3, 127 — 135
To link to this Article: DOI: 10.1080/00319107208084093
URL: http://dx.doi.org/10.1080/00319107208084093

Physics and Chemistry of Liquids. 1972. Vol. 3, pp. 127–135

Printed in Great Britain

The Hall Effect in Molten Salts

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Received February 17, 1972

Abstract—The Hall Effect is measured in the molten ionic salts CuCl, AgCl and AgBr. Values of 0.023, 0.031 and 0.027 cm^2/volt sec are obtained for the effective mobility. The values obtained are one or two orders of magnitude larger than drift mobilities and so indicate there can be no correspondence between Hall and drift mobilities in molten salts. These measurements appear to be the first of the Hall Effect in molten ionic salts.

While the electrical conduction in molten salts is of considerable technological importance, the microscopic theory of conduction is at a primitive state of development.(1) This paper demonstrates that it is possible to measure the Hall Effect in molten salt systems although the magnitude of the effect is quite small. The three salts used in this paper CuCl, AgCl and AgBr, are all considered to be ionic in nature.(2)

1. Experimental

The salts were reagent grade and were contained in quartz cells shown in Fig. 1. The cells were constructed of 4 × 7 mm rectangular quartz tubing. The current electrodes were made by welding wires to plates of the metal component of the salt. The Hall probes were made of wire with a ball of the same material at one end. The ball

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was slightly larger than the hole in the side of the cell so that some sealing was affected by holding the ball snugly against the cell wall. Wires penetrating the cell walls were potted into place and sealed with a ceramic cement which has the same thermal expansion as quartz. The molten salt was then poured into the cell through the top and filling was verified by visual inspection of the cell.

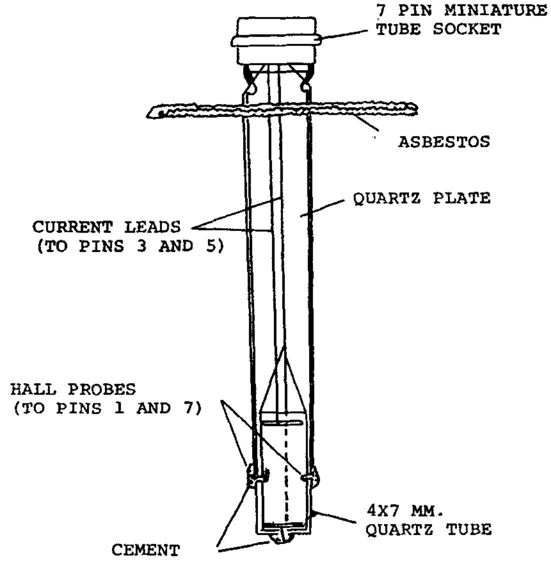

Figure 1. Details of molten salt cell. The length between the current electrodes varied from 14 mm to 20 mm. The asbestos strip served as a heat reflector to protect the preamplifiers directly above the furnace.

The use of a cell of such thickness might be questioned when compared to the cells used by Cusack *et al.*(3) in the measurements of Hall mobilities of molten metals. They report the use of cells thinner than 400 μm as being necessary to obtain reliable results using a dc method. The viscosity of these salts is similar to that of CuI which is as much as seventy times that of liquid metals.(4) The effective carrier concentration of the salts is below that of metals. While the details of the magnetohydrodynamic (MHD) forces are not understood, the influence on Hall measurements is likely to be proportional to the effective carrier concentration and inversely proportional to the viscosity. Thus, very thin cells do not seem to be necessary here. Also one advantage of the ac method is that the MHD effects are smaller.(5)

A double frequency method was used(6) as modified by Parker.(7) The current was developed by a light chopper synchronous with the line frequency at $33\frac{1}{3} = (\frac{5}{9})\ 60$ Hz while the sample was rotated at $\frac{1}{15}$ Hz. The rotation of the sample results in the sample seeing an oscillating field. The signal was amplified, filtered, and then chopped at these two frequencies so only the component at the frequency resulting from a Hall Effect survived to be displayed as a dc signal on a strip chart recorder. The various tests enumerated by McKinzie and Tannhauser(8) were applied to guard against false signals. In addition, the effects involving MHD effects coupled with rectification at contacts seem to have been absent.(9) The noise level of the resulting signal comes partly from the amplifiers and partly from instabilities within the molten salt. The sample impedances were too low for Johnson noise to be a factor in these measurements.

A small home-made furnace fits between the pole faces of a 4-in. magnet. A low ripple dc supply was used to power the furnace since electrical noise and serious mechanical vibrations resulted from current ripple interacting with the magnetic field. The temperature could reach as high as 500 °C without producing a serious temperature rise in the pole faces of the magnet. It was monitored by a platinum–rhodium thermocouple suspended near the center of the furnace. While this does not precisely measure the sample temperature, the temperature coefficients are small so that uncertainties in the temperature produce errors small compared to those from other sources.

A test against certain types of spurious signals was made with the measurement of the Hall Effect of a 1 demal solution of KCl. Aqueous solutions have a very small Hall signal that has only been measured recently.(10) We could determine that any true mobility was smaller than 4×10^{-3} cm^2/volt sec. This is an order of magnitude smaller than the values observed in molten salts. The sensitivity of the equipment was limited in this case by some extraneous noise that had none of the characteristics of a Hall signal. Presumably, MHD, evaporation, and other effects account for this noise. Similar behavior was not noted in the measurements on the molten salts.

2. Results

The results are shown in Figs. 2–4. The data show a definite proportionality to the magnetic field and, where such measurements were made, a proportionality to the applied electric field. This dependency is characteristic of the Hall Effect. The measurements on each sample were terminated due to cell failure in each case. The CuCl salt seemed to be particularly difficult to maintain within the cell. The cuprous salt also slowly decomposed as it was partially exposed to air. Since the time in which the measurement was obtained was of the order of a few minutes and the exposed surface of the salt 0.3 to 0.7 cm above the top electrode, the decomposition is believed to be unimportant.

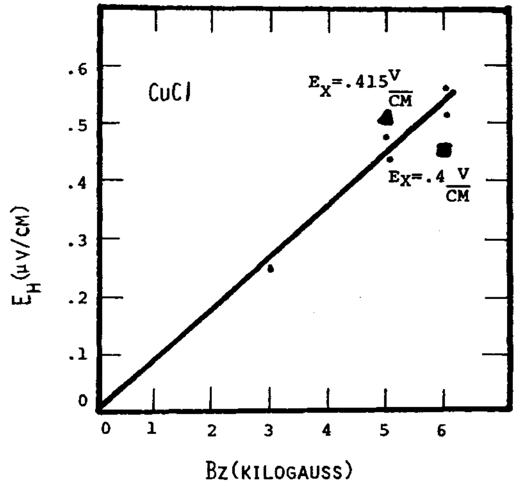

Figure 2. Hall field vs. magnetic induction intensity for CuCl. The data presented are from three different cells. The temperature of cell No. 1 (Δ) at the time of the measurement was 480 °C and the applied emf was 0.415 v/cm. The applied emf of cell No. 2 was also 0.415 v/cm but the temperature was reduced to 444 °C. At the time of measurement of cell No. 3 the temperature was 444 °C and the applied voltage was 0.4 v/cm.

The sign of the carrier is certainly positive for CuCl and is probably positive for the other two salts tested. One of the disadvantages of the ac method is the difficulty of determining the sign of the effect without error. After the measurements were completed it was

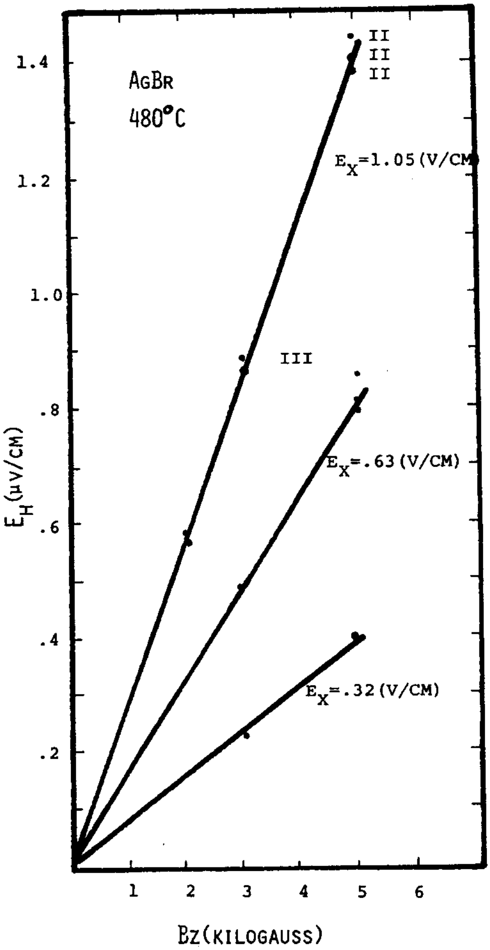

Figure 3. Hall field vs magnetic induction intensity for AgCl.

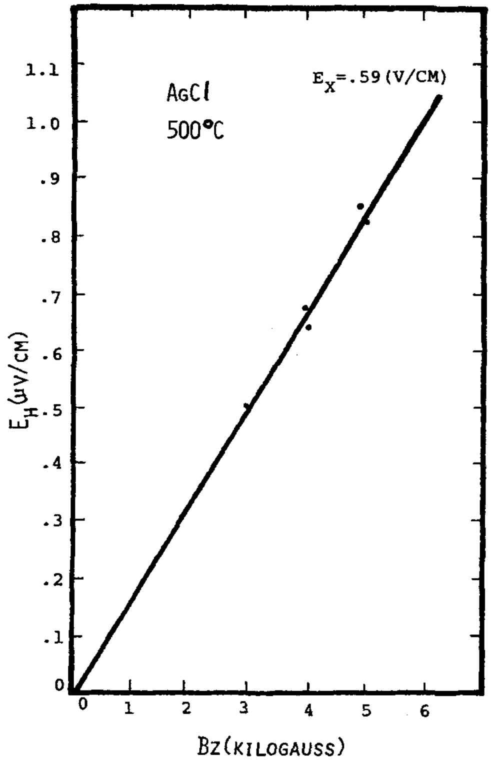

Figure 4. Hall field vs magnetic induction intensity for AgBr.

pointed out how a reversal in sign could have resulted for a particular position of a switch but a rerun of one sample confirmed the positive sign for CuCl.

Thermal power measurements made in these three salts indicated a sign generally characteristic of positive charge carriers in conformity to the sign of the Hall Effect. Allnatt and Jacobs(11) have shown theoretically that the sign of the thermal power and the Hall Coefficient do not necessarily agree for ionic solids with an excess of the metal component in solution, depending on the distribution of electrons from the excess metal. However, the authors were unable to extend their theories to say definitely that this disagreement could exist because the distribution of excess electrons is unknown and because of the greater complexity of impure crystals, in general.

The interpretation of Hall data in ionic systems has usually been discussed in terms of a simple model taken over from semiconductors. In this model, the charge carrier is assumed to move freely between rare collisions. The influence of the strong forces of the lattice between collisions is replaced by a change in effective mass of the carrier. The collisions interrupt the acceleration produced by the external field with the consequent result of a drift mobility. Simultaneously, the curvature in the path produced by the magnetic field is interrupted by the collisions resulting in a Hall mobility that is $3\pi/8$ times the drift mobility. Since both cations and anions move, it is a simple exercise to extend the model to two independently moving carriers and then to use the conductivity to deduce the separate values for each mobility.(12,13,14) This model is clearly not of use in ionic melts where the neighboring ions produce a continuous and fluctuating force on each ion.

In semiconductors, the data is often presented in terms of a Hall constant R, but we prefer to express it in terms of the Hall mobility $\mu_H = E_H/E_x B$ where E_x is the applied electric field, E_H the observed transverse field, and B is in magnetic induction intensity. The units are chosen so that μ is in terms of cm^2/volt · sec. The expression of our results in this form does not mean we believe only a single carrier is moving.

The results of our measurements are shown in Table 1. The number of cations is computed from the melt density and atomic weights. The σ values measured near the temperature of the Hall Effect measurements. The only values readily available to compare our conductivity measurements of CuCl and AgBr with are those of Grantham and Yosim.(15) The value of σ for AgCl compares well with that of Cornwell.(16) The temperature coefficient is small in these systems so for the comparison made, precisely matched temperatures are not necessary.

TABLE 1

Salt	Mobility (cm^2/volt sec)	n cations (number/cm^3)	σ (ohm^{-1}cm^{-1})	Ratio $ne\mu_H/\sigma$
CuCl	+0.023	2.2×10^{22}	3.4	24
AgCl	+0.031	2.0×10^{22}	3.9	24
AgBr	+0.027	1.8×10^{22}	3.3	23

In the last column of the table the ratio of $ne\mu_H/\sigma$ is listed. In a two carrier model based on simple semiconductor theory, this ratio should be less than one rather than the factor of 24 observed. The large value of this factor implies that the simple model based upon semiconductor concepts is not even correct as to the order of magnitude. It is likely that any model able to describe Hall Effects in ionic melts will need to be quite sophisticated to describe these interactions with the surrounding ions realistically.

The Hall Effect has been observed in a few other ionic systems. Read and Katz(18) observed the motion of cation vacancies in NaCl just below the melting point. Bullemer and Riehl,(18,19) and Rose(20) report a Hall Effect from the motion of protons in ice and Wendhausen(10) measured the Hall Effect in a number of ionic solutions.

The measurements reported in this paper can be criticized on several grounds. The salts were contaminated by the exposure to air during the filling of the cell and by some corrosion of the electrodes. The effect of impurities on these measurements is unknown. Although there are difficulties in designing suitable cells, they are not insurmountable. More information and better measured temperatures would improve our confidence in the numerical values observed. Nevertheless, we have established that Hall Effects can be detected in these systems and hence by their study one can obtain another set of clues to the mysteries in the molten salt systems.

Acknowledgements

We wish to acknowledge the assistance of Dr. Robert G. Cochran in regard to financial and technical matters and of Dr. Douglas N. Rose who helped resolve many of the mysteries of the Hall Effect Equipment.

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