

## Microwave Hall Mobility Measurements for Bovine Plasma Albumin

D. D. Eley and R. Pethig

*Chemistry Department, University of Nottingham*

The dc electronic conductivity of dry crystalline bovine plasma albumin (BPA) obeys the standard semiconduction law

$$\sigma = \sigma_0 \exp(-\Delta E/2kT)$$

with a value of  $\Delta E$  around 2.8 eV.<sup>1,2</sup> Adsorbed water increases the conductivity, lowers the value of  $\Delta E$ <sup>1</sup> (cf. also haemoglobin<sup>3</sup>) and has been shown<sup>4</sup> to act as an electron donor by its action in decreasing the conductivity of the P-type BPA-chloranil complex.

The Hall mobility measurements described here have been obtained by measurement of the room temperature conductivity and Faraday effect at 9.2 GHz. The microwave system is based upon that described by Trukhan<sup>5</sup> and incorporates a superheterodyne and phase-sensitive detection system. The specimen is placed in the centre of a cylindrical bimodal cavity operating in the TE<sub>11</sub> mode, as described by Portis and Teaney.<sup>6</sup> The attractive feature of this technique is that the electrode and inter-crystalline effects, which may enter with dc measurements on polycrystalline specimens, can be neglected.

The microwave system was calibrated for the weak field case ( $\mu B \ll 1$ ) using specimens of germanium and silicon of known conduction parameters. Room temperature measurements of the Faraday rotation in polycrystalline samples of cuprous oxide, zinc oxide and metallic selenium give Hall mobility values of 54, 90 and 32.5 cm<sup>2</sup>/v sec respectively. Our value for zinc oxide is similar to the microwave value of  $110 \pm 40$  cm<sup>2</sup>/v sec reported by Trukhan,<sup>5</sup> at the same microwave frequency. The various allotropic forms of selenium will be investigated more fully, to ascertain whether or not the observed Hall mobility of 32.5 cm<sup>2</sup>/v sec for metallic selenium is associated with conduction along the helical chains. In this way, selenium may provide a useful model for the protein  $\alpha$  helix.

The BPA Fraction V, supplied by Armour Pharmaceutical Co. Ltd., was lightly compressed into 5 mm diameter discs. When first placed in the bimodal cavity, these discs exhibit an effective ac resistivity which increases from around 10<sup>2</sup> ohm cm to 10<sup>4</sup> ohm cm over a period of three to four hours. Accurate measurements are not possible during this period, since the signal frequency cannot be locked to the resonant frequency of the loaded cavity for a sufficient length of time. This effect is reversible and is almost certainly associated with loosely bound water being driven off the protein. We expect the temperature of the specimen to rise due to dielectric heating and subsequently to fall to the ambient temperature after the water has been removed. Hydration values up to 42% by weight have been estimated for BPA Fraction V, with up to 18% by weight of this total hydration being strongly or irrotationally bound water.<sup>7</sup> On passing a steady stream of dry nitrogen through the cavity for periods up to three days, the

effective ac resistivity of some BPA specimens increases to a final steady state value around  $10^6$  ohm cm. This process is also reversible, giving further support to the conclusion that dielectric losses associated with loosely bound water, when present, determines the effective ac resistivity. Similar effects have been found for specimens of cytochrome-c and DNA, although the total resistivity changes are not nearly as large as that for BPA, indicating smaller contents of loosely bound water. The effect does not occur for specimens of cuprous oxide, zinc oxide, phthalocyanines or TCNQ complexes.

The Hall "mobility" results, obtained for the various resistivity values during the drying-out of the same BPA specimen, are given in Fig. 1. The full circles represent results obtained during a repeat run, after the specimen had been re-exposed to the atmosphere (relative humidity 18%). All the measurements were consistent with an N-type conductivity. It is a feature of the interpretation of the Faraday effect that an over-estimated value for the true effective dc conductivity of the specimen produces an under-estimated value for the Hall mobility.<sup>5</sup> Such an overestimation of the conductivity can arise if large dielectric losses, such as that due to loosely bound water, are present. This is reflected in the increasing "mobility" values of Fig. 1.

The "mobility" values were obtained from measurement of the ratio  $P_2/P_1$  of the transmitted power from the cavity to the incident power exciting the  $TE_{11}$  mode in the cavity. As expected from theory,<sup>5,8</sup> it was found that  $(P_2/P_1)^{1/2}$  was directly proportional to the magnetic field, as indicated in Fig. 2, where the symbols are associated with those in Fig. 1. Because of the finite size of the specimens and the difficulty of placing them exactly at the antinode of the electric field in the centre of the cavity, some interaction with the  $H$ -mode in the cavity occurs, resulting in possible esr absorptions. Such an absorption was indicated for the BPA specimens in the field range 0.1 to 0.5 T, giving measurements which did not lie accurately on the lines given in Fig. 2.

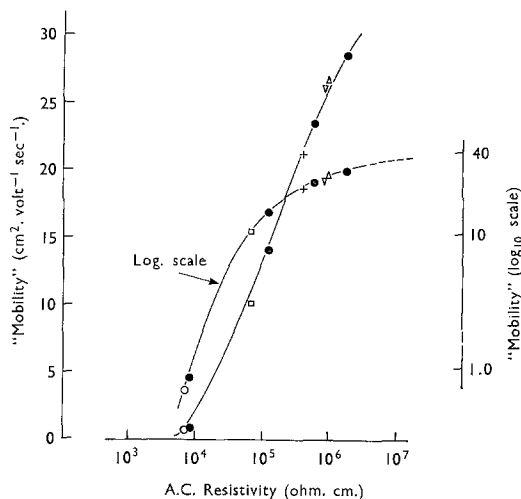


Figure 1. Variation of Hall "Mobility" with ac resistivity during the process of dehydration.

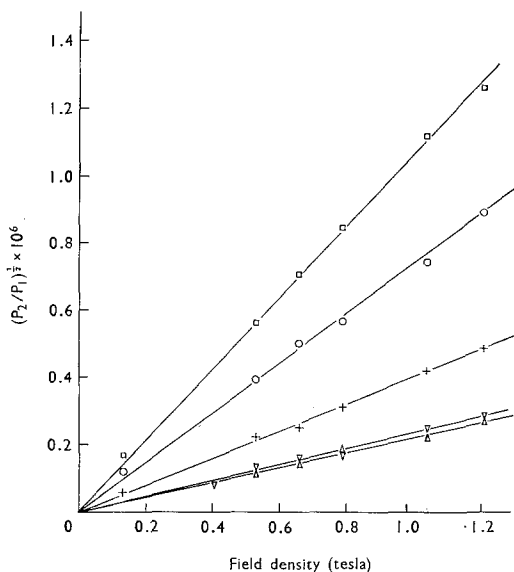


Figure 2. Variation of  $(P_2/P_1)^{1/2}$  with applied magnetic field.

The logarithmic plot given in Fig. 1 appears to extrapolate to a limiting value for the electron Hall mobility of  $40 \text{ cm}^2/\text{v sec}$  at a resistivity of around  $10^8 \text{ ohm cm}$ . This almost certainly corresponds to the situation where only the strongly and irrotationally bound water remains adsorbed on the BPA. There is no evidence for any dielectric loss associated with BPA or the strongly bound water at cm microwave frequencies,<sup>7</sup> so we can assume the value of  $10^8 \text{ ohm cm}$  to be the dc resistivity of the BPA-irrotational  $\text{H}_2\text{O}$  system. The higher value of about  $2.5 \times 10^9 \text{ ohm cm}$  for BPA—18% adsorbed water at  $20^\circ\text{C}$ , as measured in a conventional dc apparatus,<sup>9</sup> may reflect the effects of intercrystalline defects. For a mobility of  $40 \text{ cm}^2/\text{v sec}$  the resistivity of  $10^8 \text{ ohm cm}$  corresponds to an electron carrier density  $n$  of  $1.6 \times 10^9 \text{ cm}^{-3}$ . Taking the molecular weight of BPA to be  $6.65 \times 10^4$ , then from the measured specific density of the BPA discs ( $\sim 0.9 \text{ gm/ml}$ ) the density  $N$  of BPA molecules can be calculated to be  $8.25 \times 10^{18} \text{ cm}^{-3}$ . Assuming a simple charge-transfer mechanism between the water and protein, the density of injected electrons is given by

$$n = Ns \exp(-\Delta E/2kT)$$

where  $s$  is the number of charge-transfer binding sites per BPA molecule. If the maximum hydration of strongly bound water is taken as 18%, and if each bound water molecule is assumed to inject an electron into the protein (i.e.,  $s \simeq 6.7 \times 10^2$ ), then the value obtained for  $\Delta E$  is 1.5 eV. The lower limit for  $\Delta E$ , corresponding to only a single charge-transfer site per protein molecule, is 1.15 eV. These values compare reasonably with those found from dc conductivity measurements.<sup>1,3</sup> BPA Fraction V contains a significant residue of hydrophobic fatty acids. It will be of interest to investigate the electronic properties of specimens of fatty acid-poor BPA, where we would expect a smaller content of ice-like water in the hydration shell.

After prolonged drying in a desiccator, we find that the reduction in weight of BPA samples, that were previously in equilibrium with the atmosphere, ranges from 8–10%, equivalent to a loss of less than 50% of the total hydration of loosely bound water. The observed resistivity and “mobility” values for hydration values corresponding to a loss in weight of 8% are of the order  $8 \times 10^3 \text{ ohm cm}$  and  $1 \text{ cm}^2/\text{v sec}$  respectively. This would suggest that Trukhan’s mobility values<sup>8</sup> of around  $2 \text{ cm}^2/\text{v sec}$  for a series of hermetically sealed proteins (not including BPA) have been influenced by dielectric losses associated with loosely bound water. Trukhan himself clearly indicated that dipole losses could influence the results. We believe that the true value for the Hall mobility is approached only on further drying of the protein, aided by microwave action, to the stage where only irrotational water remains adsorbed. In future work, at  $\text{H}_2\text{O}$  contents greater than 34%, it may be possible for us to detect a change of sign of the Hall coefficient corresponding to the point where proton conduction through chains of water molecules begins to dominate the conductivity.<sup>9</sup> (By analogy with ice,<sup>10</sup> we expect proton Hall mobilities smaller than  $1 \text{ cm}^2/\text{v sec}$  at room temperature.)

Our main conclusion is that our measurements indicate that this particular protein system, BPA-irrotational  $\text{H}_2\text{O}$ , is capable of supporting electronic conduction with relatively large electron mobilities compatible with a well defined energy band system. We hope that further work will enable us to see if this band system is identical with that based on the hydrogen bond system, as postulated by Evans and Gergely,<sup>11</sup> and recently reviewed by one of us.<sup>12</sup>

*Acknowledgements*

We wish to thank Messrs. W. E. Porter, R. E. Parsons and A. G. Hands for their valuable work in the design and construction of the microwave system, and the Science Research Council for financial support for the project. One of us (RP) acknowledges the award of an Imperial Chemical Industries Fellowship.

*References*

1. D. D. Eley, G. D. Parfitt, M. J. Perry, and D. H. Taysum, *Trans. Faraday Soc.*, **49** (1953) 79.
2. D. D. Eley and P. W. Thomas, *Trans. Faraday Soc.*, **64** (1968) 2459.
3. B. Rosenberg, *J. Chem. Phys.*, **32** (1962) 816.
4. K. M. C., Davis, D. D. Eley, and R. S. Snart, *Nature*, **188** (1960) 724.
5. E. M. Trukhan, *Pribory tekhn. eksper.*, **4** (1965) 198.
6. A. M. Portis and D. Teaney, *J. Appl. Phys.*, **29** (1958) 1692.
7. T. J. Buchanan, G. H., Haggis, J. B., Hasted, and B. G. Robinson, *Proc. Roy. Soc. (London)*, **A213** (1952) 379.
8. E. M. Trukhan, *Biofizika*, **11** (1966) 412.
9. \* D. D. Eley and R. B., Leslie, *Electronic Aspects of Biochemistry*, B. Pullman (ed.) Academic Press, New York, 1964, p. 105.
10. B. Bullemer, H. Engelhardt, and N. Riehl, *Physics of Ice*, Plenum Press, New York & London, 1969, p. 416.
11. M. G. Evans and G. Gergely, *Biochim. Biophys. Acta*, **3** (1949) 188.
12. D. D. Eley, in: *Organic Semiconducting Polymers*, J. E. Katon (ed.), Marcel Dekker, New York (1968).

\* In ref. 9, the adsorbate concentrations in Fig. 3 are mols per  $10^3$  gm protein, not mols per  $10^2$  gm protein.