statically or by magnetic resonance. This indicates that the total of paramagnetic species, that is, a sum of both free electrons (single electrons) and sodium atoms if you have any, drops way below 50%. You may simply conclude that it is a *fast* diamagnetic species. Now the question is, does the said diamagnetic species contain sodium? Well, the transport number for sodium answers that. Sodium, regardless of concentration, moves to the cathode. If the very fast diamagnetic species contained sodium in sufficient quantity to explain the conductivity, then sodium would go to the anode. As to the explanation, it may be enough just to list that the contact repulsion between the electron and ammonia molecule is significant. This gives rise in the case of electrons in liquid helium to quite sizable effects and the electron in helium takes cavities of 18-Å size; it can give a bigger cavity in a high-pressure vapor. So the exchange repulsion is clearly there and those who have computed these things as best they could from first principles have come to the conclusion they can get repulsive interactions up to about neon in otherwise saturated electron systems. So $NH_3$ would qualify. I think in this respect the alkali metal–ammonia solutions would be in a class by themselves, because I don't know any other systems on which on this basis you would expect a repulsive interaction between the electron and the solvent. For the rest, some of the transition then would be explained in terms of a hopping mechanism but then the hopping mechanism is from singly to doubly occupied cavities. A hopping mechanism in the solvent alone would give you an increase in the limiting mobility in the first place. In the concentrated solutions you might very well have to consider cavities predominantly occupied by pairs but occasionally by singles and you get a somewhat oblique approach to the metal–nonmetal transitions which would be in some respects unique and in other respects not too unlike the ordinary.

REVIEWS OF MODERN PHYSICS VOLUME 40, NUMBER 4 OCTOBER 1968

# Microwave Dielectric Constants of Sodium–Ammonia Solutions

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Measurements have been made of the complex dielectric constant $\epsilon'-i\epsilon''$ of sodium–ammonia solutions at 10 GHz. The real part of the dielectric constant $\epsilon'$ was a very dramatic function of solution concentration. At very low concentrations $\epsilon'$ was close to the pure ammonia value, then increased slowly with concentration in the range $\chi=2\times10^{-3}$ to $\chi=2\times10^{-2}$. This increase has been attributed to the presence of permanent dipoles, and a dipole moment of approximately $10^{-16}$ esu at room temperature was determined. At $\chi=2\times10^{-2}$ the value of $\epsilon'$ decreased very abruptly to large negative values. This decrease is interpreted as the nonmetal to metal transition, indicating a very rapid decrease in the mass of the negatively charged carriers as the concentration is increased. In this same concentration range $\epsilon''$, the imaginary part of the dielectric constant, increased rapidly as would be expected from the increasing dc conductivity. Temperature-variation studies of the dielectric constant have also been made and are consistent with the known temperature behavior of the solution's conductivity, i.e., the lower the temperature the higher the concentration required to reach the metallic concentration region and hence produce a negative real part to the dielectric constant.

The nonmetal to metal transition may be readily observed in solutions of alkali metals in liquid ammonia.[1] The transition is observed from the electrical conductivity of the solutions as a function of concentration. Figure 1 shows the dc conductivity as a function of the mole fraction of sodium in ammonia. This is a composite curve extracted from the literature and interpolated to temperatures which were used in our experiments. The curves are for 25°, 0°, and −45°C. For mole fraction $\chi<2.5\times10^{-3}$ the solutions are electrolytic and exhibit a large temperature coefficient of resistance. For $\chi>2.5\times10^{-2}$ the conductivity is comparable with that of metals and the temperature coefficient of resistivity is correspondingly small. The conductivity of mercury at room temperature is approximately $10^4$ mhos/cm and that of a saturated solution of sodium in ammonia is $5\times10^3$ mhos/cm. For $2.5\times10^{-3}\leq\chi\leq2.5\times10^{-2}$ the nature of the conducting species is a subject of much controversy. The region of steepest slope in Fig. 1 is generally regarded as the nonmetal to metal transition. The transition region occurs at higher concentrations as the temperature is decreased.

In very dilute solutions the conducting species are thought to be positive metal ions and solvated electrons. A solvated electron is one which has bound to it several ammonia molecules, forming heavy negative ions. Such dilute solutions conduct electricity by an electrolytic process which involves thermally activated "hopping" of the electrons, as indicated by the large temperature coefficient of resistance. In the concentrated range the conduction mechanism is almost exclusively metallic, and the current-carrying species are well established as degenerate free electrons.[2] In the

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[1] J. C. Thompson, *Chemistry of Non-Aqueous Solvents*, J. J. Lagowski, Ed. (Academic Press Inc., New York, 1967), Vol. 2.

[2] D. S. Kyser and J. C. Thompson, J. Chem. Phys. **42**, 3910 (1965).

intermediate concentration range the current-carrying species are not well understood. The equivalent conductivity indicates the association of charged particles. Such associated particles are electrically neutral and do not contribute to the dc conductivity.

A simple model for the dielectric constant of metal-ammonia solution is

$$\epsilon' - i\epsilon'' = \epsilon_{\mathrm{NH}_3} - [\omega_p^2/\omega(\omega - i\nu)]. \qquad (1)$$

This is the Drude model, where $\omega_p^2 = ne^2/(\epsilon_0 m)$ is the plasma frequency and $\nu$ is the collision frequency between charged particles and ammonia molecules.

The object of the experiments was to determine if some behavior such as that indicated in Eq. (1) is valid and to observe how the dielectric constant is affected by the nonmetal to metal transition.

The complex microwave dielectric constant $\epsilon' - i\epsilon''$ was measured at 10 GHz using a cavity perturbation method.[3] An analysis of the cavity response both when empty and loaded with a sample permits calculation of the optical constants ($n$ and $k$) of the solution. Using Maxwell's relation $(n-ik)^2 = \epsilon' - i\epsilon''$, the real and imaginary parts of the dielectric constant can be determined. Measurements were made on solutions at temperatures of 25°, 0°, and −45°C.

Figure 2 shows the transition and high conductivity regions of the conductivity vs concentration curve. The points in Fig. 2 are those calculated from the measured values of $\epsilon''$ using the Drude relationship

$$\sigma = \epsilon'' \epsilon_0 \omega [1 + (\omega^2/\nu^2)]. \qquad (2)$$

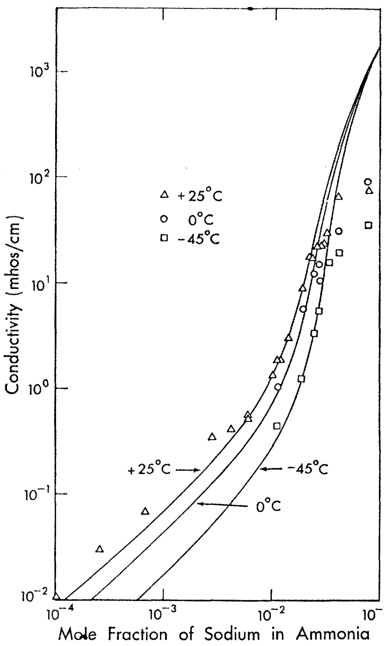

FIG. 2. Comparison between dc conductivity and Drude value calculated from imaginary part of dielectric constant.

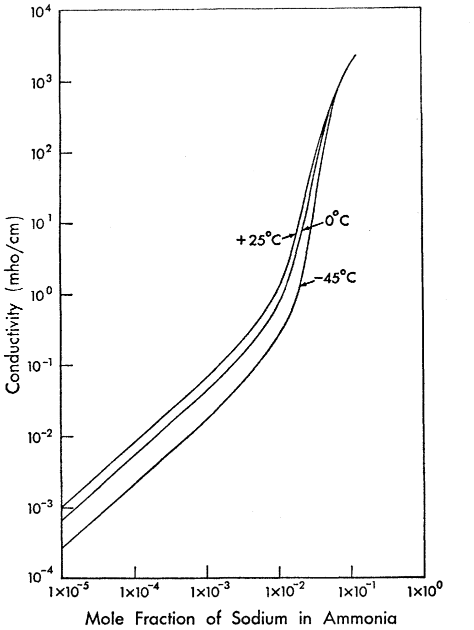

FIG. 1. Conductivity (dc) vs concentration for temperatures 25°, 0°, and −45°C.

For $\chi < 10^{-3}$ the experimental values fall above the conductivity curve. This could be due to some dielectric absorption mechanism. In the intermediate concentration range there is good agreement, while at concentrations above $\chi = 2.5 \times 10^{-2}$, the experimental points fall below the curve. This could be due to large experimental errors in this region, since the microwave skin depth is very small.

Figure 3 shows the measured values of the real part of the dielectric constant $\epsilon'$ vs mole fraction $\chi$. At very low concentrations ($\chi \sim 10^{-5}$), $\epsilon'$ is essentially equal to that of pure ammonia at room temperature. As the concentration is increased there is an indication of a decrease in $\epsilon'$. However, in the neighborhood of $\chi = 10^{-3}$, $\epsilon'$ starts to increase, reaching a value of approximately 100 at $\chi \simeq 10^{-2}$, which is followed by a very rapid decrease to large negative values at $\chi \simeq 2 \times 10^{-2}$. The region of large positive $\epsilon'$ ($\chi \simeq 10^{-3} - 10^{-2}$) is the same range in which the best agreement in Fig. 2 is achieved. It is also the concentration range in which complex species exist. The rapid decrease in $\epsilon'$ occurs near the concentration corresponding to the steepest slope in Fig. 2 and hence is believed to indicate the non-metal to metal transition.

As the temperature is decreased, higher concentrations are required to produce a negative or metallic value for $\epsilon'$. In some cases $\epsilon'$ was negative at room

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[3] C. H. Collie, J. B. Hasted, and D. M. Ritson, Proc. Phys. Soc. (London) **60**, 71 (1947).

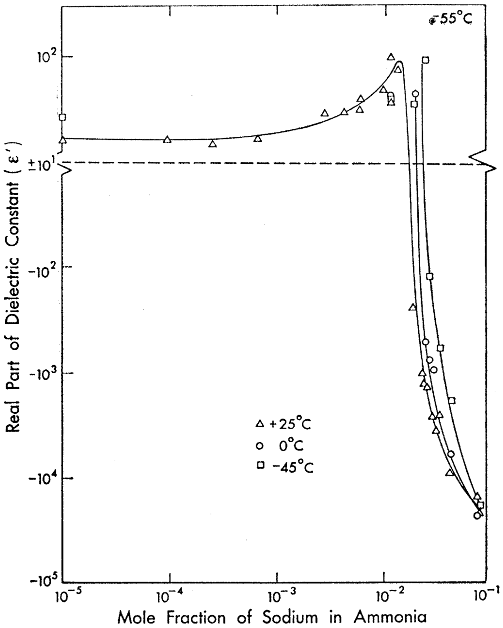

FIG. 3. Real part of dielectric constant versus concentration at 25°, 0°, and −45°C. Note the break in the ordinate.

temperature and became positive, or nonmetallic as the temperature was decreased at constant concentration.

The increase in $\epsilon'$ from $\chi = 10^{-3}$–$10^{-2}$ may be due to permanent dipoles formed by association of charged particles. It is in this concentration range that complex species are known to exist.[1] Several analyses of the concentration of complex species have been made.[4,5] Using the data of Ref. 4 the results give an average dipole moment of approximately $10^{-16}$ esu. This is the dipole moment of 2 electronic charges separated by about 20 Å, which is in reasonable agreement with a recent analysis[6] when modified to room temperature, where most of the data were taken.

From Eq. (1)

$$\epsilon' = \epsilon_{\mathrm{NH}_3}' - [\omega_p^2/(\omega^2+\nu^2)]. \qquad (3)$$

This may be modified to include the contribution of the dipoles

$$\epsilon' = \epsilon_{\mathrm{NH}_3}' - [\omega_p^2/(\omega^2+\nu^2)] + K_1[N(\chi)\mu^2/3kT], \qquad (4)$$

where $K_1$ is a constant equal to $36\pi \times 10^9$ and $N(\chi)$ is a function of solution concentration.

It is obvious that Eq. (4) will not give a good fit to the data if it is assumed that $\omega_p^2$ is simply defined as

$$\omega_p^2 = ne^2/\epsilon_0 m, \qquad (5)$$

where $n$ is the number of sodium atoms per $m^3$.

To agree with experiment $\omega_p^2$ must increase much more rapidly than $n$ at the transition. This is reasonable when one considers the value which should be ascribed to $m$, the mass of the negatively charged carriers. In the very low-concentration region, $m$ should be equal to the mass of several ammonia molecules and as the solution becomes metallic this mass decreases to that of a free electron. This is a mass reduction of the order of $10^4$ with a consequent increase of a factor of $10^4$ in $\omega_p^2$. It is indicated in Fig. 3 that this mass reduction occurs very abruptly at the generally accepted concentration.

On the metallic side of the transition the values of $\epsilon'$ are much larger numerically than would be expected from Eq. (4), which indicates that the effective mass of the electron is much less than the free value. This may be due to large experimental errors associated with the high conductivity of the solutions in this concentration range.

## Discussion of Mahaffey and Jerde's Paper

M. Pollak (University of California, Riverside): I would like to comment on a very close analogy which seems to exist between your experiments and experiments on the ac conductivity in doped semiconductors at low temperatures. In the latter case one also observes that for impurity concentrations below the metal–nonmetal transition the real part of the ac conductivity, $\sigma_{\mathrm{ac}}$, is larger [see, e.g., M. Pollak and T. H. Geballe, Phys. Rev. **122**, 1742 (1961)] than the dc conductivity, $\sigma_{\mathrm{dc}}$, and above the transition this relationship is reversed. [F. A. D'Altroy and H. Y. Fan, Phys. Rev. **103**, 1671 (1956). Table I shows the ac and dc conductivities for five samples. Samples Sb 11A and Ga 10C2 should be metallic, Ga 10C4 in the intermediate region. The frequency dependence in PN4I and PN3E is most likely due to gross inhomogeneities.] The interpretation [see, e.g., M. Pollak, Proc. Intern. Conf. Semiconductor Phys., Exeter, 1962] for the case of semiconductors is as follows: The frequency dependence below the transition region arises from the polarization inherent in conduction by hopping between inequivalent sites. The inequivalence is both in the energy of the sites and in the distances to neighboring sites. Above the metal–nonmetal transition the frequency dependence is a consequence of inertial effects associated with the rather heavy effective mass of the carriers. In the intermediate region there is a difference between your observations that $\sigma_{\mathrm{ac}}/\sigma_{\mathrm{dc}} \simeq 1$, and those in the semiconductors where $\sigma_{\mathrm{ac}}/\sigma_{\mathrm{dc}} < 1$. But the amount of experimental work in the intermediate region is very limited and the difference may simply reflect a different relationship between the microwave frequencies and the relaxation times in your experiments and in those of D'Altroy and Fan.

M. J. Sienko (Cornell): Your low-temperature data were actually below the phase separation temperature and yet I didn't see any evidence of discontinuity in the dielectric constant. The phase separation temperature in sodium is −42°C and your lowest data were at −45°C.

D. W. Mahaffey: The highest temperature at which the phase separation occurs is −42°C and this is at a mole fraction

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[4] S. Golden, C. Guttman, and R. T. Tuttle, Jr., J. Chem. Phys. **44**, 3791 (1966).

[5] E. Arnold and A. Patterson, Jr., J. Chem. Phys. **41**, 3089 3098 (1964).

[6] W. E. Millett, L. H. Dieterman, and J. C. Thompson, in *Positron Annihilation*, A. T. Stewart and L. O. Roelling, Eds. (Academic Press Inc., New York, 1967).

of $4\times10^{-2}$. At concentrations both higher and lower the phase separation temperature is lower so that in Fig. 3 only two points might be expected to be in the phase separation region. No evidence for the phase separation was observed and this may be due to the fact that the measured temperature of $-45°C$ is probably a lower limit due to the way in which it was measured. The single point at $-55°C$ in the upper right-hand corner of Fig. 3 is well within the phase separation region and its very high positive value may be an indication of the phase separation.

L. Onsager (Yale): First of all I would like to know what frequency did you use?

D. W. Mahaffey: 10 GHz.

L. Onsager: The rise of the dielectric constant is pretty big there. I'm not quite sure whether I can believe 20-Å size dipoles. One could cut it a little, of course, if the negative ion is divalent. But even so, an analogy to the semiconductor could perhaps depend a bit on hopping between cavities but a limited hopping distance at the intermediate concentration with sort of alternating hopping and ion motion. Incidentally, the effective mass of the electron is still almost certainly that of a cavity so it would be half the displaced mass of ammonia. That is, in the low-concentration end, the effective mass of the electron might be more or less given by classical hydrodynamics. The electron sits in a hole, judging from the density of the solution, and the mass is then half the displaced mass of solvent which would be, of course, only a couple of ammonia molecules. There are possibly more memory effects, by the way, than just plain dipoles, in that the system of distributions of ions around each other due to Coulomb forces at some longer distances also gives rise to a memory effect and these give rise to an apparent increase of dielectric constant and incidentally, also to a dispersion in the conductivity which would be noticeable at $10^9$ cycles. The characteristic time there is simply the Maxwell relaxation time although the spectrum is not simply Maxwellian. It is a continuous spectrum with a bottom at the Maxwell relaxation time.

D. W. Mahaffey: The single ammonia molecules have a relaxation time of about $10^{-12}$ sec. So for unbound ammonia molecules the measurements are essentially dc measurements. As regards the size of the dipole being about 20 Å, I must admit being a bit surprised when it came out so large. The species which we took into account in arriving at that dipole size were two which were mentioned by Golden, Gutman, and Tuttle in their publication and these are essentially a positive metal ion with its surrounding cloud of ammonia molecules, bound loosely to a solvated electron with its surrounding cloud of ammonia molecules and another species which was a positive sodium ion bound to a negative sodium ion. We assumed both species to have the same dipole moment and arrived at a size in the range 15–20 Å. What we would like to do, of course, is study the temperature variation more in the enhanced region, for as yet we only have data for that at room temperature. It would be interesting to see what happened to that as the temperature increased.

L. Onsager: Offhand, 20 Å is hard to believe from first principles and in conjunction with other things we know of transport properties in the solutions, which we can interpret after a fashion at least. A tentative suggestion is that the initial increment of the dielectric constant is still an effect of hopping but of a fraction which is limited because there is no second opportunity to hop. Such hopping could take place over a considerable distance and give a fairly large polarization. But I haven't followed that up in any detail.