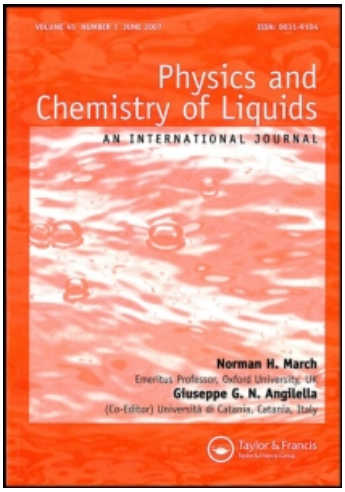

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

The determination of the dielectric constant of liquid ammonia

J. Baldwin[a]; J. B. Gill[a]
[a] School of Chemistry The University, Leeds, England

To cite this Article Baldwin, J. and Gill, J. B.(1970) 'The determination of the dielectric constant of liquid ammonia', Physics and Chemistry of Liquids, 2: 1, 25 — 28
To link to this Article: DOI: 10.1080/00319107008084075
URL: http://dx.doi.org/10.1080/00319107008084075

Physics and Chemistry of Liquids. 1970. Vol. 2, pp. 25–28

Printed in Great Britain

The Determination of the Dielectric Constant of Liquid Ammonia

J. BALDWIN and J. B. GILL‡

School of Chemistry
The University
Leeds LS2 9JT
England

Most of the information presently available on the behaviour of electrolyte solutions is confined to aqueous media at 25 °C and 1 atmosphere pressure.[1] We have initiated a programme of work to determine quantities such as electrode potentials, conductances and activities of electrolyte solutions in non-aqueous solvents. In particular, we have studied the mobilities and activities of various ions in liquid ammonia solutions within the temperature range −35° to −70 °C.

A considerable volume of this type of work was carried out between 1900 and 1940,[2] but with certain notable exceptions, such as the conductance work of Hnizda and Kraus,[3] little of this can be regarded as conforming to the high standards of accuracy required at the present day.

In the course of our recent work on the determination of activities of ions in liquid ammonia,[4] we have found it necessary to use fairly precise dielectric data for the solvent in order to examine the applicability of the Debye-Hückel equation in the calculation of activity coefficients. At the outset of our work these data were not available in the existing literature at the standard of precision which was required. Grubb, Chittum and Hunt[5] in 1936 carried out dielectric studies over the temperature range 5 °C to 35 °C; Smyth and Hitchcock[6] worked at an imprecise temperature close to −70 °C, whilst Hooper and Kraus[7] worked at the boiling point of the solvent, −33 °C, a point perhaps atypical of normal liquid ammonia. We report, therefore, the results of our own accurate determinations of the dielectric constant of liquid ammonia. It has been brought to our notice[8] that a recent survey of the temperature variation of the dielectric constant of liquid ammonia has recently been made by Burow and Lagowski[9] in which they used the heterodyne beat method. Their results are compared here with our own.

‡ Please address all correspondence to J. B. Gill.

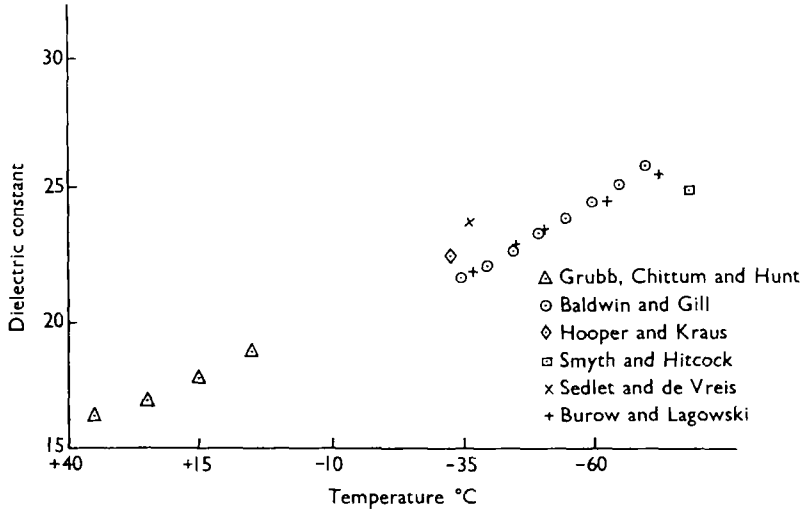

Fig. 1. Summary of available data on the dielectric constant of liquid ammonia.

Experimental

The method involved the direct comparison of the capacitance of a cell containing liquid ammonia with that of the same cell containing air at very low pressure but at the same temperature. The cell consisted of two concentric platinum cylinders (10 cm long and 1.6 cm mean diameter) mounted on glass tubing to keep them about 0.1 cm apart. The platinum connecting leads, insulated with narrow-bore glass tubing, were brought out of the neck of the cell through a soda-glass pinch seal. The cell was mounted within a glass envelope fitted with a 0.8 cm gas inlet and a narrow-bore liquid outlet. The whole assembly was shielded with aluminium foil and mounted in a stirred bath containing light silicone oil in a thermostatted refrigerator unit. Temperatures, which were regulated to within ± 0.02 °C, were measured with a platinum resistance thermometer mounted within the aluminium shielding. This shielding also contained a periscope by which the liquid level in the cell could be observed. Outside the cell the connecting leads, mounted in rigid nylon tubing shielded with aluminium, were held in a fixed position as widely apart as possible. All the shielding was well earthed.

The cell was washed with distilled water and pumped out for 48 hours at a pressure of 10^{-1} mm Hg. After this the cell was isolated from the

vacuum line. The capacitance of the cell was then determined at 5 °C intervals of temperature between 0 °C and – 70 °C as the thermostatted bath was firstly cooled and secondly warmed. Similar determinations were carried out between – 35 °C and – 70 °C after liquid ammonia had been condensed into the cell. These experiments were carried out several times and agreement in readings to within 0.1 $\mu\mu$F was obtained.

Experiments made to assess the effect of the leads and of fluctuations in the level of liquid ammonia above the platinum cylinders indicated this to be insignificant, and all experiments were subsequently carried out with the ammonia level between 0.1 and 0.2 cm above the level of the cylinders.

All the capacitances and conductance measurements were made with a Wayne Kerr B221/A. Bridge, upon liquid ammonia which had a specific conductance lower than 2×10^{-6} ohm^{-1} cm^{-1}. Below this value the capacitance of the cell did not vary significantly with the conductivity of the ammonia.

Results

Smoothed values of the dielectric constant, ϵ, of liquid ammonia, were obtained from the following results using,

$$\epsilon = \frac{\text{Capacitance of cell filled with liquid ammonia}}{\text{Capacitance of cell filled with air at low pressure}}$$

Temp. (°C)	– 70	– 65	– 60	– 55	– 50	– 45	– 40	– 35
Cap. cell at low press. ($\mu\mu$F)	51.66	15.64	51.62	51.60	51.58	51.65	51.54	51.52
Cap. cell with liq. NH_3 ($\mu\mu$F)	1339	1302	1265	1232	1200	1170	1141	1115
Dielectric const. of liq. NH_3	25.9	25.2	24.5	23.9	23.3	22.6	22.1	21.6

Consideration of the various sources of error in this work leads us to conclude that these results can be accepted as accurate to within ± 0.5%.

The above graphical comparison of our results with those presented by earlier workers indicates that our results lie in good agreement with those of Burow and Lagowski, particularly at the higher temperatures in the normal liquid range. This agreement would appear to confirm both these series of results especially as the two sets of data were obtained by tow different methods of measurement.

REFERENCES

1. Hills, G. J., *Chemistry in Britain* **6**, 268 (1969).
2. Monoszan, A. M., and Pleskov, V. A., *J. Phys. Chem.* (*USSR*) **6**, 513 (1935); Watt, G. W., Leslie, W. B., and Moore, T. E., *Chem. Revs.* **32**, 219 (1943) and references therein; Kraus, C. A., *Ann. N.Y. Acad. Sci.* **51**, 789 (1949).
3. Hnizda, V., and Kraus, C. A., *J. Amer. Chem. Soc.* **71**, 1565 (1949).
4. Baldwin, J., and Gill, J. B., *Chem. Comm.* 1537 (1968) and work to be published.
5. Grubb, H. M., Chittum, J. E., and Hunt, H., *J. Amer. Chem. Soc.* **58**, 776 (1936).
6. Smyth, C. P., and Hitchcock, C. S., *J. Amer. Chem. Soc.* **56**, 1084 (1934).
7. Hooper, G. S., and Kraus, C. A., *J. Amer. Chem. Soc.* **56**, 2265 (1934).
8. We thank the referee of this paper for drawing attention to the work of Burow and Lagowski.
9. Burow, D. F., and Lagowski, J. J., *Adv. Chem. Ser.* **50**, 131 (1965).
10. Sedlet, J., and de Vreis, T., *J. Amer. Chem. Soc.* **73**, 5808 (1951).