

function of pressure. Measurements of nonpolar liquids show this assumption to be a good one in our pressure range. Finally, there is the term $\partial(\mu_0^2 g)/\partial P$ which can be evaluated from the measured values of $\partial\epsilon_0/\partial P$ but which cannot be resolved into its component parts, $\partial\mu_0/\partial P$ and $\partial g/\partial P$, from dielectric measurements alone. It is the attempt to estimate the relative value of these two terms that is the principal goal of this paper.

The first to discuss dielectric data in the sense outlined above were Jacobs and Lawson⁸ who analyzed existing literature data, much of it from Bridgman's laboratory. For water, and in particular for some of the lower aliphatic alcohols, they concluded that the dipole moment of the molecule must decrease upon application of pressure. However, it should be noted that this conclusion is predicated on two assumptions: (1) The packing about an arbitrary reference dipole is cubic in the case of alcohols (for water they chose diamond packing), and (2) that neither the type of packing nor the extent of intermolecular association is pressure dependent. For liquids generally considered not to be associated, such as ethers and halobenzenes, Jacobs and Lawson concluded that the data could not be as readily analyzed and suggested that for these types of liquids either $\partial\mu_0/\partial P$ or $\partial g/\partial P$ could be large.

Gilchrist, Early, and Cole⁹ measured the pressure dependence (to 1 kbar) of $g\mu_0^2$ for glycerol and *n*-propanol at low temperatures. In both cases they found $\partial(g\mu_0^2)/\partial P < 0$ and in the case of glycerol they agreed with Jacobs and Lawson that the effect was probably due to pressure-induced distortion of the molecules resulting in a diminution of the dipole moment. For *n*-propanol, however, they suggested that a "more efficient packing of shorter hydrogen-bonded chains of molecules at higher pressures" was the reason for the decrease of $g\mu_0^2$ with increasing pressure, i.e., the main effect is a decrease of the correlation factor with pressure.

Recent¹⁰ measurements in this laboratory of the pressure dependence of dielectric polarization of several isomeric octyl alcohols showed that $\partial(g\mu_0^2)/\partial P$ was positive in every case, but that its magnitude depended on pressure, temperature, and most sensitively of all, on the structure of the alcohol itself. Because the effect of pressure is so temperature dependent and is also so markedly different for very similar isomers, we doubted if it could be due to a pressure-induced distortion of the molecules. Rather, we chose to interpret the results on the basis of a

constant dipole moment and ascribed all of the pressure dependence to a variation of the correlation factor. However, the fact that $\partial(g\mu_0^2)/\partial P$ appeared to change sign if the temperature was sufficiently reduced and the pressure increased (see Fig. 6 of Ref. 10; similar observations were noted by Jacobs and Lawson for ethanol but were not discussed further) suggested that this was an oversimplification and led to the investigation reported in this paper.

EXPERIMENTAL

Instrumentation

The three-terminal, coaxial dielectric cell used for high-pressure studies has been described elsewhere.¹⁰ It was modified to the extent that a ceramic pin, screwed into the bottom guard ring, acted as a piston guide to keep the "high" electrode reproducibly centered. With this arrangement the cell constant determined at atmospheric pressure after a run agreed with the initial value to better than 0.01%. The cell constant was corrected for the compression of the "low" (guarded) electrode at elevated pressures.

Capacitance was measured with a General Radio Type 1615A bridge. In the dipole-moment studies, where the conductance of the hexane solutions was very low, a resolution of 0.0001 pF out of a total of about 30 pF was easily achieved. For the experiments with pure liquids such precision was neither possible nor required, of course, and a precision of 0.1% was considered adequate.

Data were obtained on both the increasing and decreasing portion of the compression curve, with excellent agreement. Because $de/dt \approx -0.002 \text{ deg}^{-1}$ for *n*-hexane at atmospheric pressure, the pressure was always changed slowly and about 1 h was allowed for the adiabatic heat of compression to be dissipated in the dipole-moment studies. The capacitance, rather than the thermocouple EMF, was the most sensitive thermometer.

Bridgman's¹¹ syphon bellows technique was used to measure the compression of the 6-methyl-3-heptanol. The bellows was calibrated at room conditions to obtain the change in volume per unit longitudinal compression. Trial runs with methanol, 3-octanol, and *n*-hexane demonstrated that we could reproduce literature data.

Solutions were prepared by weight with suitable precautions to avoid errors due to selective vaporization etc. Solution densities were determined pycnometrically and an Abbe refractometer was used to measure n_D . The determination of the index of refraction is the least precise aspect of our dipole-moment experiments.

⁸ I. S. Jacobs and A. W. Lawson, *J. Chem. Phys.* **20**, 1161 (1952).

⁹ A. Gilchrist, J. E. Early, and R. H. Cole, *J. Chem. Phys.* **26**, 196 (1957).

¹⁰ G. P. Johari and W. Dannhauser, *J. Chem. Phys.* **48**, 5114 (1968).

¹¹ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1958); *Proc. Am. Acad. Arts Sci.* **68**, 1 (1933).