value of the dielectric constant of pure *n*-hexane was fit to a third-order polynomial in pressure and it was assumed that the coefficients of this polynomial would also apply for n_D^2 of the dilute hexane solutions, i.e., the pressure dependence of the molar refraction was assumed the same as that of the Clausius–Mosotti function of the pure solvent. The required densities were those measured by Eduljee, Newitt, and Weale[16] and we assumed the compression of the dilute solutions identical to that of the pure solvent.

The results of these experiments are shown in Fig. 4. For diethyl ether the apparent slight dependence of μ_0 on pressure is within experimental error and we believe that $\partial\mu_0/\partial P=0$ for $P<4$ kbar.

The results for *sec*-butanol are less clearcut: because of the necessity to work at very low concentrations in order to avoid association of the alcohol,[13] a condition which presumably becomes even more stringent at high pressures, our experimental uncertainties are sufficiently large that we hesitate to ascribe numerical significance to the apparent increase in μ_0. However, we do believe that the results are adequately well defined to assert that the dipole moment probably *increases* slightly with pressure, a conclusion opposite to Jacob and Lawson's speculation.

We were then interested in studying a molecule where the effect of moderate pressure on the dipole moment might be large. Williams,[17] from an investigation of the pressure dependence of the dielectric constant of bulk poly(methylmethacrylate), proposed that its dipole moment increases as a result of pressure-induced conformational changes. A simple molecule for which rotation about a C–C bond will lead to changes in the dipole moment is 1,2-dichloroethane, whose temperature-dependent polarization has received extensive attention.[18] Consequently, we measured the polarization of dilute solutions of this solute in *n*-hexane at constant temperature as a function of pressure. These experiments were conducted in the concentration range where our experimental precision is good[19] and we believe that this is a real effect—the first that has been reported as far as we know.

The next question is: is the increase in μ_0 of dichloroethane due to conformational changes or is it due to changes in the C–Cl group moment itself? To test this we determined the dipole moment of *n*-butyl chloride and found that the dipole moment remains essentially constant, the seeming slight decrease not being considered significant (Fig. 4). It is probably too naive to expect that this result can be extended directly to the dichloroethane, but it does lend weight to the suggestion that there is a real effect in the increase noted for dichloroethane. Parenthetically, we note that $\partial(g\mu_0^2)/\partial P<0$ for amyl chloride (insert to Fig. 1) which is thus construed to be due to an increased antiparallel alignment of near-neighbor dipoles with increasing pressure. Some of our preliminary experiments with CH_3CN indicate a similar effect if it can be assumed that the dipole moment is constant.

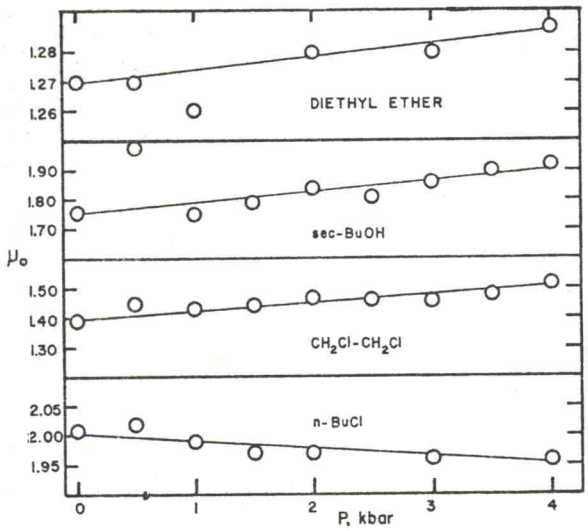

FIG. 4. Dipole moment as a function of pressure at 30°C.

Finally, one may question if the effect is due to a distortion of the polar solute molecule or whether it may not be an indirect effect due to the change in dielectric constant of the solvent. Most theories which attempt to relate the dipole moment in solution, μ, to its value in vacuum, μ_0, rely on some sort of cavity model as proposed by Onsager.[20] By assuming a spherical cavity of essentially the molecular volume and by further assuming the medium outside this cavity to be dielectrically uniform, Onsager showed that the reaction field, which acts to induce an additional moment in the molecule inside the cavity, was given by

$$R=\tfrac{1}{3}(8\pi N)\,[(\epsilon-1)/(2\epsilon+n^2)]\,[(n^2+2)/3]\,\mu.$$

The dielectric constant of *n*-hexane at 30°C increases from 1.8714 at atmospheric pressure to 2.1425 at 4 kbar, so the relative change in reaction field is large. Because Onsager's theory is at best an approximation, it might be that much of the observed effect is indirectly due to a change in the solvent property rather than a "direct" distortion of the

[16] H. E. Eduljee, D. M. Newitt, and K. E. Weale, J. Chem. Soc. 1951, 3086.

[17] G. Williams, Trans. Faraday Soc. 60, 1556 (1964).

[18] M. V. Volkenstein, *Configurational Statistics of Polymer Chains* (Interscience Publishers, Inc., New York, 1963), Chap. 3 especially; S. Mizushima, *Structure of Molecules and Internal Rotation* (Academic Press Inc., New York, 1954).

[19] At 1 atm we obtain $\mu_0=1.39$ D. Under the same conditions, Mizushima[18] obtained $\mu_0=1.37$ D. A. L. McLellan [*Tables of Experimental Dipole Moments* (W. H. Freeman and Co., San Francisco, Calif., 1963)] quotes $\mu_0=1.38$ D for these conditions.

[20] L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936); C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier Publ. Co., Amsterdam, 1952).