Pressure Dependence of Molecular Dipole Moment

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THE study of dielectric polarization of fluids under hydrostatic pressure has recently[1-3] received renewed attention. Results of such studies have not only intrinsic interest, but are important for an understanding of all chemical processes carried out under pressure. The most general analysis of the equilibrium dielectric polarization of polar fluids is that of Kirkwood and Fröhlich.[4] Jacobs and Lawson[5] have shown that the pressure dependence of the dielectric constant, using the Kirkwood–Fröhlich formulation, depends on the term $\mathrm{d}(g\mu_0^2)/\mathrm{d}P$. Here, μ_0 is the dipole moment of the molecule in vacuum and g, the Kirkwood correlation factor, is a measure of specific intermolecular forces resulting in preferred near-neighbour dipole–dipole orientations, *i.e.* it is a measure of the liquid structure.

It is not possible to resolve $g\mu_0^2$ by dielectric measurements of pure liquids. Jacobs and Lawson assumed that the short-range liquid structure remains unchanged upon application of pressure and suggested that $\mathrm{d}\mu_0/\mathrm{d}P > 0$ for diethyl ether, for example. From the known force constants it appears that pressure-induced distortion of molecules, leading to a change in their dipole moment, is quite feasible energetically and dielectric absorption of non-polar molecules[6] and pressure-induced changes in electronic[7] and i.r.[8] spectra have been rationalized on this basis. However, as far as we know, there have been no previous attempts to actually measure the dipole moment as a function of pressure. We report the first results of such a study.

The dielectric constant of dilute solutions of diethyl ether in n-hexane was studied at 30° at pressures to 4 kbar. The cell has been described elsewhere;[3] a General Radio type 1615A admittance bridge was used. Data were analyzed by the simplified Guggenheim method as detailed by Smith[9] in which the essential parameter is $\epsilon - n^2$. We have assumed that the molar refraction, $[(n^2 - 1)/n^2 + 2)]\rho^{-1}$, has the same pressure dependence as the Clausius–Mossotti function, $[(\epsilon - 1)/(\epsilon + 2)]\rho^{-1}$. Here, ρ is the density of the solution which is assumed to have the same compressibility as pure hexane; the latter was obtained by interpolation of Eduljee's[10] data. The Figure is a graph of our experimental results; the linearity of the curves and their smooth extrapolation to the solvent value at all pressures is a measure of the internal consistency of the data. At atmospheric pressure, we obtain the result $\mu_0 = 1{\cdot}27$ D [lit.[11] from 1·15 D (gas phase) to 1·30 D (in benzene)] and we find this to be independent of pressure. If this result is valid for pure diethyl ether it implies that $\mathrm{d}g/\mathrm{d}P > 0$, *i.e.* that near-neighbour dipoles assume an increasingly parallel alignment upon application of pressure.

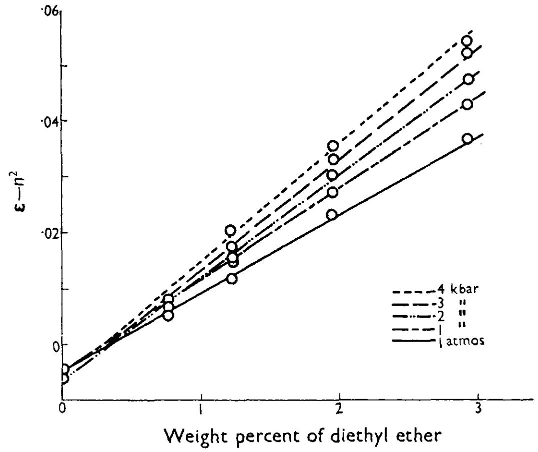

FIGURE. *Graph of* $\epsilon - \mathrm{n}^2$ *as a function of* w, *the weight percent of diethyl ether in n-hexane at* 30°. *Diameter of circles is a measure of the experimental uncertainty with* $\Delta\rho = \pm\ 0{\cdot}0001$ *and* $\Delta\epsilon = \pm\ 0{\cdot}0001$.

Whether our results can be generalized to other types of molecules awaits further experiments, now in progress. We note that for most fluids $(\partial E/\partial V)_{\mathrm{T}} > 0$ for $P \lesssim 7$ kbar but changes sign at higher pressures where severe distortion of molecules ultimately must occur. Measurements of the dipole moment at these pressures should be a useful method of studying intermolecular interactions in condensed phases.

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[1] E. Whalley, in "Advances in High Pressure Research", ed. R. S. Bradley, Academic Press, New York, 1966, p. 172.

[2] J. F. Skinner, E. L. Cussler, and R. M. Fuoss, *J. Phys. Chem.*, 1968, **72**, 1057.

[3] G. P. Johari and W. Dannhauser, *J. Chem. Phys.*, in the press.

[4] J. G. Kirkwood, *J. Chem. Phys.*, 1939, **7**, 911; H. Fröhlich, "Theory of Dielectrics", Oxford University Press, London, 1949.

[5] I. S. Jacobs and A. W. Lawson, *J. Chem. Phys.*, 1952, **20**, 1161.

[6] H. S. Gabelnick and H. L. Strauss, *J. Chem. Phys.*, 1967, **46**, 396.

[7] A. H. Kadhem and H. W. Offer, *J. Chem. Phys.*, 1967, **47**, 1289.

[8] J. Reynolds and S. S. Sternstein, *J. Chem. Phys.*, 1964, **41**, 47.

[9] J. W. Smith, *Trans. Faraday Soc.*, 1950, **46**, 394.

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

[11] A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, 1963.