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Study of the Pressure Dependence of Dielectric Polarization*

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The pressure dependence of the dielectric polarization of polar fluids depends principally on three factors: (1) the fluid density, which is easily measured; (2) pressure-induced distortion of molecules, expressed as $d\mu_0/dP$; and (3) pressure-induced changes in the liquid structure, expressed as dg/dP, where g is Kirkwood's dipole correlation factor. $d(g\mu_0^2)/dP$ has been determined over a wide range of temperature to 4 kbar for *n*-propanol, *sec*-butanol, and 6-methyl-3-heptanol and is found to be either positive or negative depending on the temperature and the specific nature of the alcohol. At temperatures and pressures where g is near unity, increasing pressure enhances $g\mu_0^2$ because of pressure-induced chain association; when g is already large, increasing pressure decreases $g\mu_0^2$. Determination of the dipole moment in dilute hexane solution as a function of pressure shows that for diethyl ether and *n*-butyl chloride, μ_0 is virtually constant to 4 kbar, μ_0 of *sec*-butanol probably increases slightly, and μ_0 of 1,2-dichloroethane increases by about 6%. The decrease of $g\mu_0^2$ of alcohols with increasing pressure is attributed to interchain correlations as the packing in the liquid approaches that of the crystal.

INTRODUCTION

The availability of commercial equipment has spurred interest in a wide variety of high-pressure experiments. Thermodynamic studies have received much attention[1] because the effect of pressure on equilibria is well founded, i.e., $\partial\Delta G/\partial P=\Delta V$. The theory of transport processes and chemical reactions is less certain, and the effect of pressure is usually discussed in some form of the activated complex picture due to Eyring and his colleagues. Formally, the pressure coefficient of a chemical rate constant is expressed as a volume of activation, and much speculation[2] has been generated to rationalize the various results on a qualitative molecular basis. Whalley,[3] in an excellent review, suggests that the volume of activation may be resolved into two components: $\Delta V_r^\ddagger$, "the change in volume due directly to the changing interaction of the reacting molecules with one another, and $\Delta V_s^\ddagger$ which is the change of volume due directly to the changing interaction of the reacting molecules with the solvent." As regards $\Delta V_s^\ddagger$, Whalley demonstrates that electrostatic interactions due to ions, dipoles, and higher multipoles ultimately depend on the pressure coefficient of the dielectric constant, among other factors. Analogous statements apply to ΔV of reaction, of course. Thus, a study of the type reported here will provide order-of-magnitude data for a general analysis of rate and equilibrium experiments.

In addition to the utility outlined above, dielectric measurements have intrinsic interest because they provide a sensitive indicator of intermolecular interactions. The most general treatment of dielectric polarization in liquids is that due to Kirkwood[4] and Fröhlich[5] which yields the equation

$$\epsilon_0=\epsilon_\infty+\left(\frac{3\epsilon_0}{2\epsilon_0+\epsilon_\infty}\right)\left(\frac{\epsilon_\infty+2}{3}\right)^2\frac{4\pi N\rho}{3MkT}\mu_0^2 g. \qquad (1)$$

Here ϵ_0 is the equilibrium permitivity, a measure of the total polarization; ϵ_∞, the "high-frequency" permitivity characteristic of induced polarization, is often approximated by n_D^2 or a simple function thereof in lieu of more precise knowledge; M is the molecular weight; ρ is the liquid density; μ_0 is the dipole moment of the molecule measured in vacuum; g is the dipole correlation factor first introduced by Kirkwood. The correlation factor is essentially a measure of the correlation of orientation of near-neighbor dipoles: g's greater than unity are to be interpreted as being due to a predominantly parallel alignment while g's less than unity indicate antiparallel alignment. We have demonstrated in previous investigations[6,7] that an analysis of the correlation factor as it depends on temperature and molecular structure is a fruitful source of information about intermolecular interactions in the liquid state, especially so for systems with strong, angle-dependent, interactions such as hydrogen-bonded liquids.

The isothermal pressure dependence of the equilibrium permitivity, as shown by differentiation of Eq. (1), is a composite of three terms. $\partial\rho/\partial P$ can be measured directly. $\partial\epsilon_\infty/\partial P$ can be estimated adequately from the Clausius–Mossotti equation on the assumption that the molar polarization is not a strong

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