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.

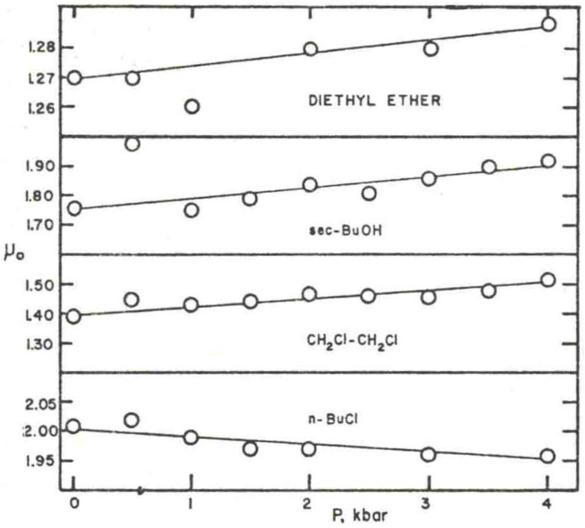

FIG. 4. Dipole moment as a function of pressure at 30°C.

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.

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

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

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

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[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).

solute molecules. To test this possibility, we determined the dipole moment of 1,2-dichloroethane in decalin at 30° and atmospheric pressure to be $\mu_0=1.42$ D. Under these conditions the dielectric constant of the decalin is 2.165, almost the same as that of *n*-hexane at 4 kbar. Consequently, while solvent changes due to pressure may have a small effect, we believe that the major part of the increase in dipole moment of dichloroethane is due to a pressure-induced distortion of the molecule which favors the *gauche* conformation.

To summarize this aspect of the work, we can say that the effect of pressure on the dipole moment is probably small for most molecules for $P<4$ kbar, and for alcohols it is likely to be negligible compared to the observed variation of $\partial(\mu_0^2 g)/\partial P$. Bridgman's compressibility experiments[11] show that $(\partial E/\partial V)_T>0$ for most liquids for $P<7$ kbar but upon further compression $(\partial E/\partial V)_T$ changes sign. Presumably, for $P>7$ kbar the molecules themselves are being distorted and we anticipate that $\partial\mu_0/\partial P$ will become significant in this pressure range.

We must then explain the observed decrease in $g\mu_0^2$ at low temperatures and moderate pressures as being due to a change in the correlation factor opposite in direction to that due to intermolecular chain formation. Gilchrist's[9] suggestion regarding a more efficient packing at high pressure seems to us a reasonable one. Beginning with Kirkwood,[4,14] all attempts to evaluate the correlation factor of alcohols have focused attention on the correlation between a reference dipole and its neighbors *in the same chain*, the implicit assumption being made that the rapid breaking and reforming of hydrogen bonds will cancel out possible correlations between molecules in adjacent chains. In crystalline alcohol the parallel intrachain alignment must be cancelled by an antiparallel interchain alignment in order that there be no net electric polarization. As the pressure on the liquid is increased, chainwise association is favored and undoubtedly the average packing approaches that of the solid. We suggest that the onset of this rather extensive short-range order is reflected in the decrease of the correlation factor with pressure.

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Thermal Diffusion in the Nonpolar–Polar System Helium–Methyl Chloride

A. K. Ghosh, S. K. Deb, and A. K. Barua
Indian Association for the Cultivation of Science, Calcutta-32, India

(Received 29 August 1968)

The thermal diffusion factor α_T for a 1:1 mixture of He and CH_3Cl has been measured by the two-bulb method at different temperatures ranging from 338°–530°K. The composition dependence of α_T for this system has also been studied at 362.8°K. For the temperature dependence of α_T the agreement between experimental and calculated values is poor even when inelastic collisions are taken into account. For the composition dependence of α_T the theoretical and experimental curves run approximately parallel to each other over the whole composition range. This probably means that the inelastic collisions do not play a significant role in the thermal diffusion phenomenon of this system.

I. INTRODUCTION

The calculated values of the transport properties of nonpolar gases have been found to have better accord with the experimental observations than those for the polar gases. This is mainly due to the long-range angle-dependent part of the intermolecular potential between two polar molecules which also makes the probability of inelastic collisions high. The intermolecular potential for polar molecules is generally represented by the Stockmayer or 12–6–3 potential[1] which contains the angle-dependent dipole–dipole interaction term varying as r^{-3}. However, in evaluating the collision integrals required for the calculation of the transport properties approximations are made so that effectively a spherically symmetric potential is used.

Monchick and Mason[2] have calculated the collision integrals for the 12–6–3 potential by assuming that the relative orientation of the dipoles does not change during a collision and that all relative orientations are equally probable. For most molecules at ordinary temperatures the rotational energy is much less than the translational energy which is of the order of kT. Consequently, when this condition is valid inelastic collisions should have little effect on the trajectories of the colliding molecules. This approximation should hold reasonably well for transport properties like diffusion and viscosity which to the first approximation are not affected by

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[1] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), hereafter referred to as MTGL.

[2] L. Monchick and E. A. Mason, J. Chem. Phys. **35**, 1676 (1961).

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Study of the Pressure Dependence of Dielectric Polarization*

Tunli Chen,† Walter Dannhauser, and Gyan P. Johari‡
Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

(Received 23 October 1968)

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: $\Delta V_r^‡$, "the change in volume due directly to the changing interaction of the reacting molecules with one another, and $\Delta V_s^‡$ which is the change of volume due directly to the changing interaction of the reacting molecules with the solvent." As regards $\Delta V_s^‡$, 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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† Present address: Chemistry Department, National Taiwan University, Taipei, Taiwan.

‡ Present address: Chemistry Department, Princeton University, Princeton, N.J.

[1] S. D. Hamann, "Chemical Equilibria in Condensed Systems," in *High Pressure Physics and Chemistry*, R. S. Bradley, Ed. (Academic Press Inc., New York, 1963), Vol. 2.

[2] For a recent review see W. J. le Noble, J. Chem. Educ. 44, 729 (1967) and references cited there.

[3] E. Whalley, Advan. Phys. Org. Chem. 2, 93 (1964).

[4] J. G. Kirkwood, J. Chem. Phys. 7, 911 (1939).

[5] H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, New York, 1949), 1st ed.

[6] W. Dannhauser, J. Chem. Phys. 48, 1911 (1968).

[7] W. Dannhauser and L. W. Bahe, J. Chem. Phys. 40, 3058 (1964).

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[9] A. Gilchrist,
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[10] G. P. Johari
(1968).

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 Lawson[8] 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 Cole[9] 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.

Recent[10] 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 $d\epsilon/dt\approx-0.002\ \text{deg}^{-1}$ 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's[11] sylphon 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 until 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 pycometrically 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.

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

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

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

TABLE I. Equilibruim dielectric constant as a function of temperature and pressure.

P (kbar)	ϵ_0								
T(°K)	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
n-Propanol									
361.3	12.66	13.37	14.07	14.69	15.27	15.77	16.18	16.54	16.84
303.2	19.70	20.61	21.27	21.82	22.28	22.71	23.16	23.48	23.86
273.1	24.21	24.93	25.62	26.23	26.73	27.16	27.57	27.98	28.36
244.5	29.22	30.04	30.72	31.28	31.78	32.25	32.67	33.06	33.34
224.8	33.22	33.96	34.57	35.13	35.66	36.17	···	···	···
216.0	35.36	36.03	36.62	37.16	37.62	···	···	···	···
208.0	37.42	38.2	38.9	39.5	···	···	···	···	···
sec-Butanol									
367.9	7.01	8.21	8.93	9.51	9.98	10.33	10.68	10.99	11.29
325.3	11.75	12.54	13.20	13.74	14.22	14.66	15.10	15.50	15.85
307.1	14.85	16.00	16.82	17.50	18.03	18.49	18.90	19.27	19.62
272.5	21.15	22.03	22.74	23.20	23.76	24.14	24.49	24.81	25.12
247.1	26.38	27.09	27.70	28.19	28.60	29.01	29.37	29.66	···
221.0	32.52	33.11	33.60	34.04	34.42	34.68	···	···	···
6-Methyl-3-heptanol									
364.2	3.79	4.08	4.31	4.52	4.71	4.89	5.03	5.16	5.29
333.9	4.10	4.49	4.83	5.11	5.38	5.65	5.89	6.11	6.32
304.4	4.58	5.20	5.85	6.39	6.91	7.41	7.84	8.22	8.63
274.2	5.97	7.49	8.78	9.98	11.00	11.87	12.59	13.16	13.71
258.4	7.97	10.10	11.74	13.02	14.12	14.96	15.65	16.27	16.82
243.4	11.34	13.69	15.31	16.60	17.61	18.35	18.98	19.43	19.85
236.7	12.50	15.10	16.74	17.90	18.86	19.58	20.11	20.55	20.85
229.2	15.30	17.27	18.88	20.05	20.88	21.47	21.96	22.33	22.60
217.5	18.25	20.01	21.39	22.35	23.01	23.40	23.7	···	···

Samples

Alcohols were reagent, or better, grade. 6-Methyl-3-heptanol (Chemical Samples Company) was 98% pure as received. Each alcohol was refluxed for several hours over CaH_2 and then subjected to a careful fractionation. The GC analyses showed only trivial amounts of impurities.

1,2-Dichloroethane was chromatoquality (Matheson, Coleman and Bell) and was used without further purification. *n*-Butyl chloride (Fisher, certified quality) was fractionated before use. The density and index of refraction of both compounds agree well with literature values.

n-Hexane was Matheson, Coleman and Bell chromatoquality, (99.5+%; major impurity is methylcyclopropane) used without further purification after tests showed its dielectric constant to be the same as carefully dried, 99.9+% pure, samples. All of the solvent for one solute came from the same lot of material.

Decalin (Distillation Products Industries, mixture of isomers) was distilled from CaH_2. Its density at 27° was 0.8820 g/ml; $n_D{}^{25}=1.4727$; $\epsilon_0(30°)=2.165$.

RESULTS

Pure Alcohols

The equilibrium dielectric constant of *n*-propanol, *sec*-butanol, and 6-methyl-3-heptanol was measured as a function of pressure and temperature. Isothermal data were plotted on a large scale as a function of pressure. Interpolated data are listed in Table I. The only data available for comparison are Gilchrist, Earley, and Cole's[9] for *n*-propanol: our values of ϵ_0 at 1 kbar extrapolate to 43.8 at 191°K (their highest temperature), about 2% higher than their result. At

TABLE II. Parameters for the density equation[a] for 6-methyl-3-heptanol. $\rho(P, t) = \rho(P, 0) - A(P)t$.

	P (kbar)								
	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
$\rho(P, 0)$	0.8345	0.8630	0.8827	0.8997	0.9136	0.9256	0.9366	0.9441	0.9518
$10^4 A(P)$	7.20	6.06	5.32	4.90	4.52	4.22	4.06	3.62	3.38

[a] P is the pressure in kilobars; t is in degrees Centigrade.

our lowest test temperatures, dielectric dispersion became evident as a frequency-dependent conductance from which we estimated the relaxation time on the basis of the Debye equation. Our data at 1 kbar extrapolate smoothly to those of Gilchrist, Earley, and Cole.

The isobaric density of 6-methyl-3-heptanol was found to be a linear function of temperature according to the equation

$$\rho(P, t) = \rho(P, t=0) - A(p)t. \tag{2}$$

Pertinent values of the parameters $\rho(P, 0)$ and $A(P)$ are listed in Table II.

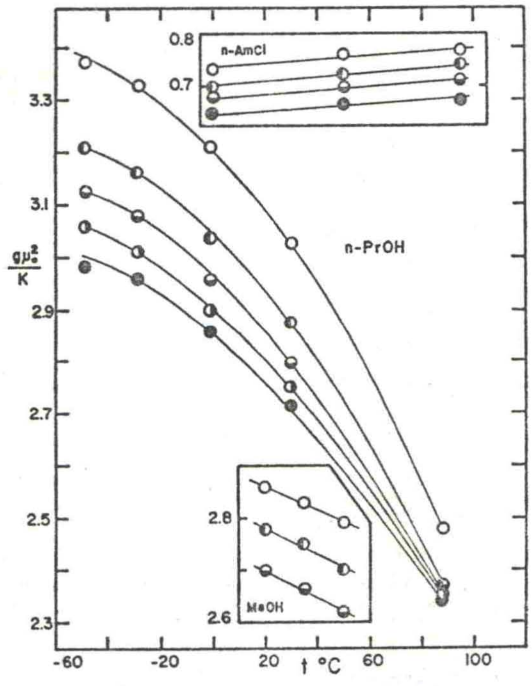

FIG. 1. $g\mu_0^2/K$ as a function of temperature at various pressures. n-propanol. $K = 1.68^2$. ○ = 1 atm; ◐ = 1 kbar; ◒ = 2 kbar; ◑ = 3 kbar; ● = 4 kbar. n-amyl chloride (top insert). Dielectric data from W. L. Lees, Ph.D. thesis, Harvard University, Cambridge, Mass., 1949; density data from P. W. Bridgman, Ref. 11. $K = 2.12^2$. ○ = 1 atm; ◐ = 1 kbar; ◒ = 2 kbar. ● = 4 kbar. Methanol (bottom insert). Dielectric data of H. Hartmann, A. Neumann, and G. Rinck, Z. Physik. Chem. (Frankfurt) 44, 204 (1965); density data from Ref. 11. $K = 1.68^2$. ○ = 1 atm; ◐ = 1 kbar; ◒ = 2 kbar.

Hexane Solutions

The dielectric constant of several dilute solutions of each solute in n-hexane was determined to 4 kbar at 30°±0.5°. In the subsequent analysis of the data the important parameter is the slope of a plot of $(\epsilon - n_D^2)$ as a function of Q. Here ϵ is the dielectric constant and n_D is the index of refraction of a solution containing Q weight-percent solute. An example of our results with diethyl ether have been reported in a preliminary Note[12]; the precision for butyl chloride and dichloroethane is similar. However, for *sec*-butanol much lower concentrations of solute were required in order to eliminate spurious effects due to solute association, a factor which presumably becomes even more important at high pressures. The maximum concentration was 0.3%[13] and the data scattered considerably. Consequently, conclusions regarding the pressure dependence of the dipole moment of *sec*-butanol are less certain than for the nonassociating solutes.

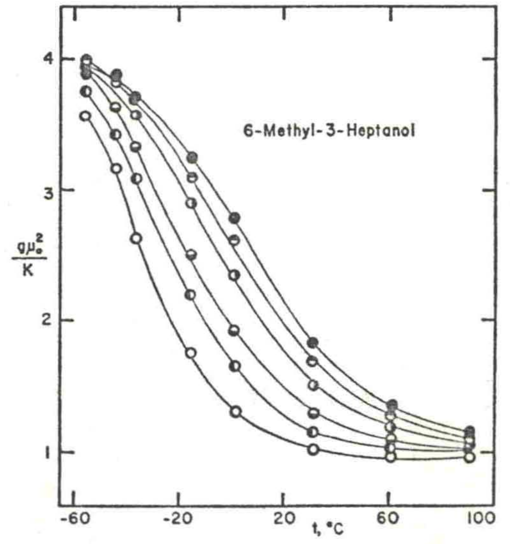

FIG. 2. $g\mu_0^2/K$ as a function of pressure at various pressures for 6-methyl-3-heptanol. $K = 1.68^2$. ○ = 1 atm; ◐ = 0.5 kbar; ◒ = 1 kbar; ◑ = 2 kbar; ◓ = 3 kbar; ● = 4 kbar.

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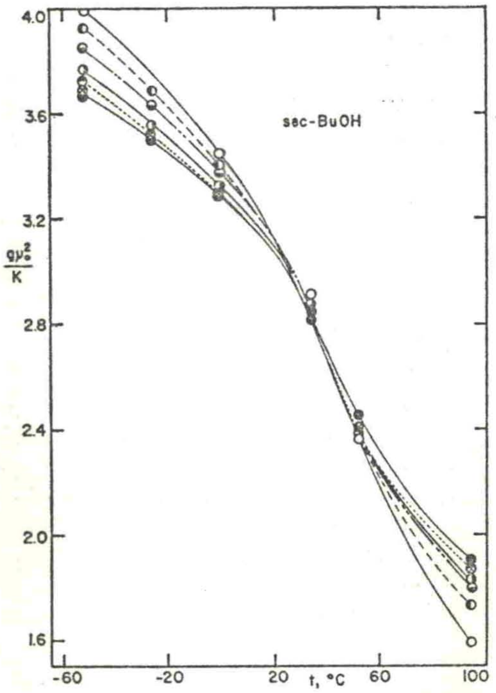

FIG. 3. $g\mu_0^2/K$ as a function of temperature at various pressures for *sec*-butanol. $K=1.68^2$. ○ =1 atm; ◐=0.5 kbar; ◒=1 kbar; ◑=1.5 kbar; ◓=2 kbar; ⊗=3 kbar; ● =4 kbar.

DISCUSSION

The quantity $g\mu_0^2/K$ was calculated as a function of temperature and pressure for *n*-propanol, *sec*-butanol, and 6-methyl-3-heptanol from our experimental results. For propanol and *sec*-butanol, the densities were estimated from Bridgman's[11] data by linear extrapolation: Bridgman's 1-kbar data for *n*-propanol at 30° and 75°C extrapolate to Gilchrist's[9] values at low temperatures and we assumed that similar extrapolations would work at higher pressures. Furthermore, we used Bridgman's isobutanol density data since his and our own experience has shown that alcohol isomers have nearly the same compressibility and temperature coefficient of density. The constant K was chosen to equal μ_0^2, using 1.68 D as the best estimate of μ_0 for aliphatic alcohols. Thus, if μ_0 were constant, the curves show the variation of g. The results of these calculations are shown in Figs. 1–3.

Our results for *n*-propanol are that $\partial(\mu_0^2g)/\partial P<0$ over the entire range of temperature and pressure, but it appears that the pressure dependence would change sign at higher temperatures. In the vicinity of room temperature, *n*-propanol and methanol (insert to Fig. 2) are similar, as are most of the lower aliphatic primary alcohols. It was this sort of behavior that prompted Jacobs and Lawson to suggest that $\partial\mu_0/\partial P<0$.

For 6-methyl-3-heptanol, the pressure dependence is just the inverse of that of propanol: at all temperatures and pressures $\partial(\mu_0^2g)\partial P>0$ but it appears that the derivative would change sign if we could extend our measurements to *lower* temperatures and/or higher pressures. These results are qualitatively similar to those already reported[10] for other octanol isomers.

On the basis of our previous work, it had become apparent that $\partial(\mu_0^2g)/\partial P$ was greatest for those alcohols whose –OH group was relatively hindered by being situated near the middle of the alkyl group and by being surrounded by (branch) methyl groups, viz., 5-methyl- or 2-methyl-3-heptanol. For these compounds, the Kirkwood correlation factor is close to unity at room temperature and atmospheric pressure. We propose that under such circumstances, the predominant effect of increasing pressure is to favor intermolecular association via hydrogen bonding to form chain *n*-mers. At first the average correlation factor increases rapidly as the degree of association increases, but g approaches an asymptotic[14] value for infinitely long chains. Thus, once the chains have attained a moderate size, further chainwise association will not be reflected in the correlation factor. It is with the onset of this size that $\partial(g\mu_0^2)/\partial P$ appears to change sign, the exact temperature and pressure of sign reversal depending in a sensitive manner on the geometry of the alcohol monomer.

In order to test this idea we wanted to investigate a liquid whose correlation factor was close to unity near its normal boiling point and which reached its asymptotic value (at 1 atm) at not too low a temperature for our high-pressure equipment. A perusal of some of our previous results[7] indicated that *sec*-butanol should be suitable, and the results illustrated in Fig. 3 show this indeed to be true. For this compound we are able to measure the reversal of sign of $\partial(g\mu_0^2)/\partial P$ hinted at in the propanol and octanol results.

It is clear from these results that there are at least two pressure-dependent processes involved in determining $\partial(g\mu_0^2)/\partial P$ and we suggest that at relatively high temperatures and low pressures, where chain association is small, the principal contribution comes from an increase of the correlation factor with increasing pressure due to enhanced chain association.

What then is the cause for the reversal is sign of $\partial(g\mu_0^2)/\partial P$ at relatively low temperatures and high pressures? In order to test whether the dipole moment does change with pressure, we determined the dipole moment of several polar solutes in dilute *n*-hexane solution. The dielectric constant data were analyzed according to the simplified Guggenheim method according to Smith.[15] Unlike the procedure used in evaluating g from Eq. (1), it is now no longer adequate to consider the molar refraction to be independent of pressure. The experimentally determined

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