

### Conclusion

The photocurrent quantum efficiency of dibenzothiophene, determined from 14 sandwich cells, varies between  $10^{-7}$  and  $10^{-8}$  electrons/quantum. Under similar experimental conditions, highly photoconductive anthracene gave values ranging between  $10^{-6}$  and  $10^{-8}$  electrons/quantum. This comparison must be considered tentative primarily due to the inherent uncertainty in the measurement of the photoconductivity data. Furthermore, the melt-cooled anthracene photo-cells are more uniform and show better electrical contacts. The solution fluorescence quantum efficiency of dibenzothiophene ( $\phi_F = 0.025$ ) is about  $1/10$ th of anthracene ( $\phi_F = 0.23$ ).<sup>29</sup> From the relationship  $\tau_n = \tau_e/\phi_F$  where  $\tau_n$  is the mean lifetime in the absence of all other competitive process and  $\tau_e$  is the actual lifetime, one can estimate  $\tau_e = 0.2$  nsec for dibenzothiophene<sup>30</sup> which is an order of magnitude smaller than anthracene ( $\tau_e = 4.5$  nsec).<sup>31</sup> Thus the differential significance of the crystal photoconductivity and

the fluorescence lifetime or efficiency of the solution is not obvious.

On the other hand, the lack of fluorescence in the crystal of zone-refined dibenzothiophene implies that the photoconduction is not severely influenced by the fluorescence quenching features present in the solid state. Since there was no detectable photocurrent in the 410–500-m $\mu$  region, the involvement of triplet states in the carrier generation process may also be eliminated. In this respect dibenzothiophene resembles rubrene, which although an excellent photoconductor does not fluoresce in the crystal form.<sup>32</sup>

(29) Measured in ethanol. We are indebted to Dr. S. Ness for these values.

(30) Calculations based on ethanolic solution:  $\tau_n = 3.47 \times 10^8 r^2 n^2 \int \epsilon dr$ .

(31) A. S. Cherkasov, V. A. Molchanov, T. M. Vember, and K. G. Voldaikina, *Sov. Phys.-Dokl.*, **1**, 427 (1956).

(32) M. Kleinerman, L. Azarraga, and S. P. McGlynn, *J. Chem. Phys.*, **37**, 1825 (1962).

## The Effect of Pressure on the Density and Dielectric Constant of Polar Solvents

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A technique has been developed for the simultaneous determination of density and dielectric constants of liquids at high pressure. This employs a bellows dilatometer attached to a linear differential transformer and containing the guarded capacitor of a heterodyne beat dielectric device. Data are reported for five polar solvents—chlorobenzene, ethyl acetate, isopropyl ether, tetrahydrofuran, and dichloromethane—at 30 and 50° and at pressures up to 5000 atm. The results are fit to various correlating equations.

The effect of pressure on the properties of solvents is important not only as a clue to the structure of the liquid state but is also invaluable in the interpretation of solvent interactions with various solute molecules. For example, high-pressure kinetic studies provide a formidable tool for the study of chemical reactions in solution, but interpretation of the results requires a knowledge of the variation of density and dielectric constant with pressure. Then the results can be used for mechanistic interpretations,<sup>1</sup> the determination of the structure and properties of the transition state,<sup>2</sup> and for the prediction of solvent effects on reaction rates.<sup>3,4</sup> In this work we report an experimental technique for

the simultaneous determination of density and dielectric constant of liquids at pressures up to 5000 atm. New results for these quantities are reported for five polar solvents, and these data are compared with several analytical expressions proposed in the literature.

The classical relationship for expressing the pressure dependence of the molar volume  $v$ , is the Tait equa-

- (1) R. A. Grieger and C. A. Eckert, *J. Amer. Chem. Soc.*, **92**, 2918 (1970).
- (2) K. F. Wong and C. A. Eckert, *Trans. Faraday Soc.*, in press.
- (3) C. A. Eckert, *Ind. Eng. Chem.*, **59**, 20 (1967).
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tion,<sup>5</sup> usually written in terms of the compression  $k$  as

$$k = \frac{v_1 - v_p}{v_1} = C \log \left( \frac{B + P}{B + 1} \right) \quad (1)$$

where  $v_1$  and  $v_p$  are the molar volumes at 1 atm and at pressure  $P$ , respectively, and  $B$  and  $C$  are constants. The constant  $B$  is a function of the substance and of temperature, but not of pressure. Attempts have been made to relate it to internal pressure.<sup>6</sup> For many substances, the same value of  $C$  has been found, invariant with both pressure and temperature. Recently, new derivations of the Tait equation have been worked out<sup>7</sup> which indicate that it may have some basis in theory.

The dielectric constant  $\epsilon$  has also been correlated by a Tait-like expression<sup>8</sup>

$$1 - \frac{\epsilon_1}{\epsilon_p} = A \log \left( \frac{B + P}{B + 1} \right) \quad (2)$$

where  $B$  is the Tait constant for density and  $A$  is a pressure-independent constant. If both eq 1 and 2 are valid, then the compression is linear in the reciprocal of dielectric constant.

$$k = \frac{C}{A} \left( 1 - \frac{\epsilon_1}{\epsilon_p} \right) \quad (3)$$

Other authors<sup>9</sup> have used eq 2 as a two-parameter expression, determining both constants  $A'$  and  $B'$  empirically

$$1 - \frac{\epsilon_1}{\epsilon_p} = A' \log \left( \frac{B' + P}{B' + 1} \right) \quad (4)$$

Skinner, Cussler, and Fuoss<sup>9b</sup> proposed a similar expression, substituting dielectric susceptibility for dielectric constant

$$1 - \left( \frac{\epsilon_1 - 1}{\epsilon_p - 1} \right) = A'' \log \left( \frac{B'' + P}{B'' + 1} \right) \quad (5)$$

where  $A''$  and  $B''$  are constants to be fit. Recent comparisons of the results of using various expressions have been presented by Hartmann, *et al.*,<sup>9a</sup> and Schadow and Steiner.<sup>10</sup>

The need to determine the effect of pressure on both density and dielectric constant has become more apparent recently, especially in terms of the above relationships. Some authors have determined both, but not simultaneously.<sup>9b,11</sup> One example of a simultaneous determination was that of Brown,<sup>12</sup> but at pressures only up to a few hundred atmospheres. A similar apparatus was used by Mopsik<sup>13</sup> to 2000 atm. In this work we describe a somewhat different type of apparatus which has been used up to 5000 atm.

### Apparatus

The experimental apparatus consisted of a variable-volume high-pressure sample cell, containing a dielectric constant cell, all of which fit inside the cavity of a

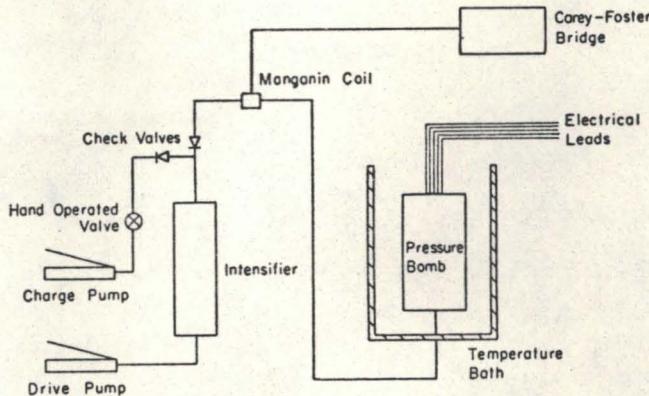


Figure 1. High-pressure system and thermostat.

thermostated high-pressure bomb. Electrical leads into the bomb permitted simultaneous measurement of dielectric constant, by a heterodyne beat technique, and of sample density, by electrical determination of the displacement of an iron core in a transformer inside the bomb.

**A. High-Pressure System.** A schematic diagram of the high-pressure rig is shown in Figure 1. The pressure generating system consisted of hand pumps, intensifier, and a manganin coil pressure gauge, all constructed by Harwood Engineering Co. The system was rated at 200,000 psi and a Carey-Foster bridge was used to measure pressures, with a resolution of 25 psi up to 100,000 psi. The pressure bomb, also by Harwood, was constructed of two concentric, shrink-fitted, auto-frettaged Martensitic steel cylinders, with an overall diameter of 10 in. and a length of 16 in. The available working space was 1.5 in. in diameter by 6 in. long. The pressure transmitting fluid was a 5:1 mixture of white gas and di-( $\alpha$  ethyl hexyl) sebacate (Esso's Univis P-38).

The entire bomb was mounted in a 25 gallon temperature bath (containing Wesson oil plus 1% hydroquinone as antioxidant) controlled and measured to  $\pm 0.02^\circ$  by thermometers with calibration traceable to

(5) P. G. Tait, "Physics and Chemistry of the Voyage of the H. M. S. Challenger," Vol. II, Part, IV, 1888.

(6) (a) R. E. Gibson and J. T. Kincaid, *J. Amer. Chem. Soc.*, **60**, 511 (1938); (b) R. E. Gibson and O. H. Loeffler, *J. Phys. Chem.*, **43**, 207 (1939).

(7) (a) R. Ginell, *J. Chem. Phys.*, **34**, 1249 (1961); (b) G. A. Neece and D. R. Squire, *J. Phys. Chem.*, **72**, 128 (1968).

(8) (a) B. B. Owen and S. R. Brinkley, *Phys. Rev.*, **64**, 32 (1943); (b) B. B. Owen and S. R. Brinkley, *J. Chem. Educ.*, **21**, 59 (1944).

(9) (a) H. Hartmann, A. Neumann, and G. Rinck, *Z. Phys. Chem. (Frankfurt am Main)*, **44**, 218 (1965); (b) J. F. Skinner, E. L. Cussler, and R. M. Fuoss, *J. Phys. Chem.*, **72**, 1057 (1968).

(10) E. Schadow and R. Steiner, *Z. Phys. Chem. (Frankfurt am Main)*, **66**, 105 (1969).

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(12) R. F. Brown, Jr., *J. Res. Natl. Bur. Std., Sect. C*, **67**, 33 (1963).

(13) (a) F. I. Mopsik, *ibid., Sect. A*, **71**, 287 (1967); (b) F. I. Mopsik, *J. Chem. Phys.*, **50**, 2559 (1969).

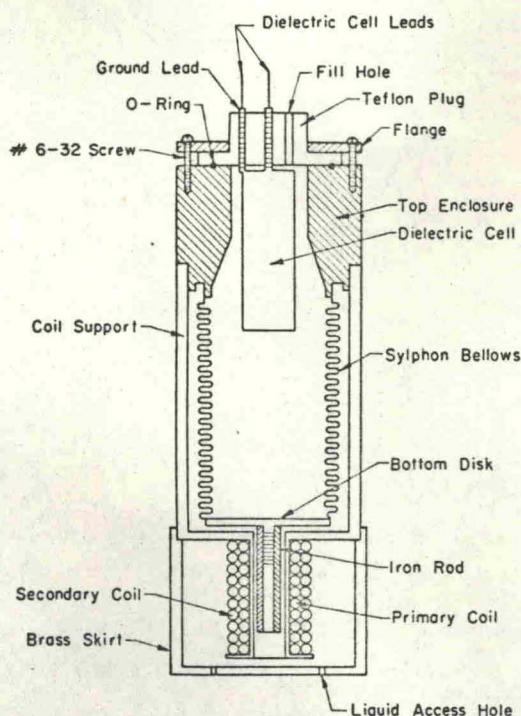


Figure 2. High-pressure density and dielectric constant cell.

the National Bureau of Standards. Further details of the high-pressure system are given elsewhere.<sup>14</sup>

**B. High-Pressure Cell.** The high-pressure cell, shown in Figure 2, had an internal volume of about 27 cm<sup>3</sup>, variable by the expansion of a Sylphon bellows. Attached rigidly to the base of the bellows was a 1 1/2 in. long piece of 1/4-in. soft iron rod, as a core for the transformer. The 1 1/8-in. phosphorbronze bellows had an inside diameter of 5/8 in. and a length of 2 3/8 in. With 22 active corrugations it was rated for a maximum compression of 1 1/8 in. This bellows was soldered to the top enclosure, which was drilled out to provide space for the dielectric cell, well away from the moving end of the bellows. The sample chamber was closed by a Teflon plug, sealed by a CNR-nitroso rubber O-ring, and covered by a coating of epoxy glue.

Integral with the high-pressure cell shown at the bottom of Figure 2 was a variable transformer for determination of the position of the bellows. The coils were wound on a thin brass cylinder, slit to reduce eddy current losses. The primary coil was wound first with five layers of No. 32 Formvar-coated copper wire. The secondary coil was wound directly over the primary coil, again with five layers of the same wire. Both coils were wound at 80 turns per inch per layer. The dc resistance of the primary coil was 14.5 ohms; that of the secondary coil was 14.7 ohms. Before winding the coils the central shaft was coated with Teflon tape to reduce the possibility of rubbing the insulation off the wires. Each coil when completed was lightly covered with glue. This was sufficient to hold the wires in place and prevent unwinding. A protective brass skirt

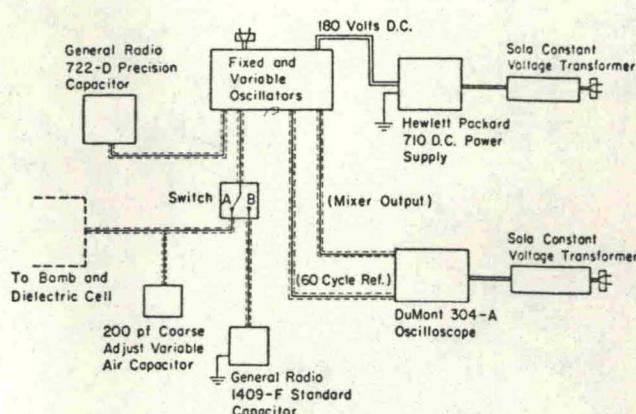


Figure 3. Heterodyne beat apparatus for dielectric constants.

was soldered to the coil support to form a rigid unit.

The dielectric cell was mounted inside the high-pressure cell by means of a threaded spindle on the inner cylinder screwed into the Teflon plug. The spindle served as the "hot" electrical lead to the dielectric cell, and a threaded rod placed through the plug was the ground lead.

This cell consisted of two precision-machined ( $\pm 0.0002$  in.) concentric brass cylinders, both rigidly supported by and electrically insulated by two high-strength ceramic rings, made from McDanel 3/8-in. (Av 30) high-temperature alumina, with a compressive strength of 400,000 psi. The working dielectric gap was 0.3008 in. i.d. and 0.3550 in. o.d. by about 2 in. long. To protect against spurious effects from the movement of the bellows, the bottom of the dielectric cell was protected by a brass guard skirt.

**C. Dielectric Constant Apparatus.** The dielectric constants were measured by the heterodyne beat technique,<sup>15</sup> which compares the frequency of a fixed, crystal-controlled reference oscillator with that of a variable oscillator. A schematic of the apparatus is shown in Figure 3.

The oscillator unit was that described by Gerteis.<sup>16</sup> The 180-V power supply for it was a Hewlett-Packard Model 710 dc power supply. The oscilloscope used was a DuMont 304-A model. The output from the mixer circuit was placed in the Y axis of the scope while a 60 cps reference frequency was put into the X axis. The line voltage to both the dc generator and oscilloscope was stabilized against voltage fluctuations by Sola constant voltage transformers. The precision measuring capacitor was a General Radio 722-D variable air capacitor. The high range (200–1150 pF) used could be read directly to  $\pm 0.1$  pF and estimated to  $\pm 0.02$  pF. The high range was calibrated by the University of Illinois Physics-Betatron Laboratory to better than

(14) S. P. Sawin, M.S. Thesis, University of Illinois, Urbana, 1968.

(15) L. Hartshorn and W. H. Ward, *J. Inst. Elect. Engr. (London)*, 79, 597 (1936).

(16) R. L. Gerteis, Ph.D. Thesis, University of Illinois, Urbana, 1963.

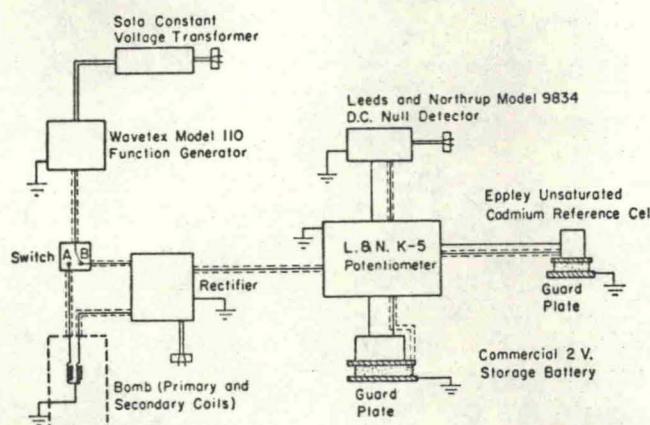


Figure 4. Schematic of apparatus for density measurements.

$\pm 0.01\%$ . To eliminate inaccuracies due to frequency drift a low-capacity switch was placed in the probe line to permit checking with a General Radio 1409-F standard capacitor, which had a thermal- and time-insensitive 1000 pF rating.

All electronic equipment was properly grounded and thermally protected by surrounding with  $1/2$ -in. styrofoam sheeting. All cables were coaxial (as indicated by dotted lines in the drawings) and were connected with UHF connectors. The lead into the pressure bomb was quite rigid to prevent geometrical changes, and completely shielded.

**D. Density Measuring Apparatus.** The technique used to measure density changes under pressure is related in part to that developed by Doolittle, Simon, and Cornish.<sup>17</sup> The motion of a ferromagnetic rod inside a cylindrical transformer due to compression of the material within the cell produced a changing voltage in the secondary coil. *A priori* calibration of the coils then allowed one to translate the voltage change into a linear displacement and subsequently into volume and density changes. A schematic of the apparatus for density measurements is shown in Figure 4.

The signal source was a Wavetek Model 110 function generator. The operating conditions were set to maximize voltage amplitude and frequency stability as well as the sensitivity of the coil assembly, while the current flux through the coils was sufficiently small to minimize heating. The signal used was a 3000-cps sine wave with amplitude 3.3 V. A constant voltage transformer and thermal insulation held the amplitude stability to better than  $\pm 0.05\%$  for short term usage (10 min) and  $\pm 0.25\%$  for long term usage (24 hr). The dc offset control was periodically adjusted to ensure zero dc voltage through the primary coil.

For better accuracy, the ac output voltage was rectified and measured potentiometrically. The rectifier, based on two balanced Nexus operational amplifiers in a linearizing circuit, provided an output of sufficient stability to introduce no additional uncertainties into the signal.

The dc measuring device used was a Leeds and Northrup 7555 Type K-5 potentiometer. On the high (0–1.6 V) range used, the input signals could be read to  $\pm 5 \mu\text{V}$  with an accuracy of 0.003%. Auxiliary equipment for the potentiometer included a Leeds and Northrup Model 9834 guarded dc null detector, an Eppley unsaturated cadmium constant voltage reference cell, and a 2 V dc power supply.

In Figure 4 the solid lines enclosed by two dashed lines represent coaxially shielded cable. All connections were of the BNC type except for binding posts on the potentiometer circuits. The two "hot" leads from coils within the bomb were soldered to BNC connectors which were rigidly fastened to a grounded plate held directly above the bomb. There were no visible effects due to any type of stray voltage pickup.

The null detector, reference cell, and power supply were all guarded against leakage voltage by using coaxial cable for the (+) lines, with the outer shielding of the cable connected to the guard post of the potentiometer. The reference cell and power supply were rested on guard plates consisting of aluminum–plexiglass–aluminum sandwiches. The other end of the guard plate was attached to the top aluminum sheet, and the bottom sheet was connected to an earth ground.

Since the function generator unit did have a slight variation of output amplitude, both the voltages to the primary coil and from the secondary coil were monitored, and the quantity measured was the voltage ratio ( $V_{\text{sec}}/V_{\text{pri}}$ ) by the switching arrangement shown in Figure 4. The voltage ratio was time invariant and depended only upon the geometrical configuration of the coil–rod assembly.

Further details of the apparatus are given elsewhere.<sup>18</sup>

#### Procedure

Fischer reagent grade chlorobenzene was treated with 5% potassium carbonate solution to remove acids. It was then washed twice and fractionally distilled from Linde 4-A molecular sieves in a 1-in. column 36 in. long packed with glass helices. The boiling range was 131.4–131.6°.

Atmospheric densities were measured at 30 and 50° in a constant-temperature water bath using modified Sprengel pyrometers. The pyrometers were calibrated against water and had volumes of approximately 10 cm<sup>3</sup>. Weighings with and without liquid samples were made on a Mettler H-6 balance. Duplicate runs were made on each material and the results were reproducible to within  $\pm 0.0001 \text{ g/cm}^3$ .

The dielectric cell was calibrated by measuring its capacity when filled with a series of materials of varying dielectric constant, and the edge effects were found to be

(17) A. K. Doolittle, I. Simon, and R. M. Cornish, *AICHE J.*, **6**, 153 (1960).

(18) L. G. Schornack, M.S. Thesis, University of Illinois, Urbana, 1969.

quite small.<sup>18</sup> The initial dielectric constants at 30° were measured relative to dry nitrogen, and the initial dielectric constants at 50° were calculated from the change in cell capacity with temperature.

The high-pressure cell was carefully cleaned and dried before each run. The dielectric liquid was weighed into the cell to an accuracy better than 0.05%, and the cell was sealed. The initial atmospheric point was taken after allowing the cell to reach equilibrium over a 3-4-

highest pressures used.<sup>14</sup> Thus under the worst possible conditions, the residual temperature error due to the heat of compression would be of order 10<sup>-5</sup>°. In every case equilibrium was further assured by the constancy of both the density and dielectric measurements for at least 30 min before a data point was recorded.

Most data points were taken during the cycle of increasing pressure. The pressure was increased at the rate of about 1000 psi/min. Data points were taken

Table I: Experimental Results for Dielectric Constant and Density

Solvent	Data at 30°			Data at 50°		
	P, atm	ε	ρ, g/cm <sup>3</sup>	P, atm	ε	ρ, g/cm <sup>3</sup>
Chlorobenzene	1	5.552	1.0960	1	5.216	1.0630
	461	5.798	1.1280	1135	5.648	1.1362
	1355	6.050	1.1733	2407	5.946	1.1977
	1933	6.175	1.1978	3701	6.173	1.2441
	2955	6.445	1.2358	5029	6.363	1.2831
	4046	6.561	1.2715			
Ethyl acetate	1	5.984	0.8883	1	5.422	0.8642
	508	6.297	0.9271	624	5.792	0.9124
	1031	6.522	0.9634	1111	5.991	0.9444
	2075	6.884	1.0151	2075	6.308	0.9951
	3054	7.152	1.0508	3010	6.559	1.0315
	4070	7.392	1.0811	4026	6.828	1.0618
Isopropyl ether	5029	7.598	1.1048	5060	7.027	1.0881
	1	3.805	0.7129	1	3.519	0.6924
	524	4.216	0.7606	451	3.884	0.7349
	1054	4.515	0.7957	1007	4.176	0.7760
	2044	4.916	0.8418	1923	4.528	0.8230
	3020	5.229	0.8747	3034	4.858	0.8637
Tetrahydrofuran	4009	5.508	0.8998	4036	5.105	0.8919
	5016	5.767	0.9241	5046	5.339	0.9163
	1	7.261	0.8730	1	6.272	0.8320
	461	7.605	0.9021	612	6.614	0.8765
	1054	7.941	0.9345	1250	6.917	0.9148
	1566	8.195	0.9592	2512	7.473	0.9686
Dichloromethane	2095	8.414	0.9814	3674	7.920	1.0033
	2965	8.750	1.0126	5102	8.419	1.0368
	3995	9.153	1.0376			
	5057	9.461	1.0632			
	1	8.649	1.3078	40	7.757	1.2587
	178	8.860	1.3325	205	7.939	1.2716
	697	9.298	1.3886	502	8.239	1.3087
	959	9.524	1.4103	747	8.451	1.3279
	1342	9.770	1.4387	1057	8.673	1.3506
	2048	10.171	1.4893	1446	8.923	1.3852
	3074	10.708	1.5505	1963	9.198	1.4219
	4063	11.159	1.5963	2685	9.550	1.4658
	4883	11.545	1.6276	3491	9.878	1.5064
				4280	10.167	1.5401
				5121	10.439	1.5725

hr period. For each succeeding point approximately 1.5 hr equilibrium time was allowed for each 500-atm pressure increase. The thermal time constant (temperature half-life) of the contents of a similar cell within the same bomb had been found previously to be about 3 min at atmospheric pressure and about 5 min at the

after equilibration at approximate values of 1, 500, 1000, 2000, 3000, 4000, and 5000 atm at each temperature. In addition, several points were taken during the cycle of decreasing pressure, the 1-atm point always being repeated. The pressure was dropped as slowly as possible to prevent cracking of the epoxy coating on the

seal and subsequent leaking. The pressure cycle at 30° was run first, followed by the 50° pressure cycle on the same sample of liquid.

### Results and Discussion

The density and dielectric constants of five polar solvents—chlorobenzene, ethyl acetate, isopropyl ether, tetrahydrofuran, and dichloromethane—were measured at pressures up to 5000 atm at 30 and 50°. The experimental results are given in Table I, and the chlorobenzene data are compared with previously reported literature values in Figures 5 and 6. The densities are in excellent agreement with those reported by Skinner, *et al.*,<sup>9b</sup> and the dielectric constant values lie very close to both those of Skinner, *et al.*,<sup>9b</sup> and Hartmann, *et al.*,<sup>19</sup>

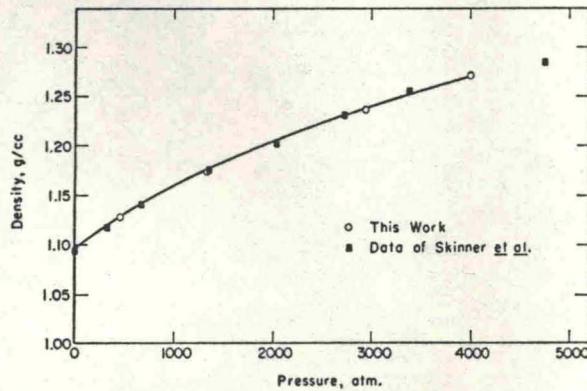


Figure 5. Density of chlorobenzene as a function of pressure at 30°.

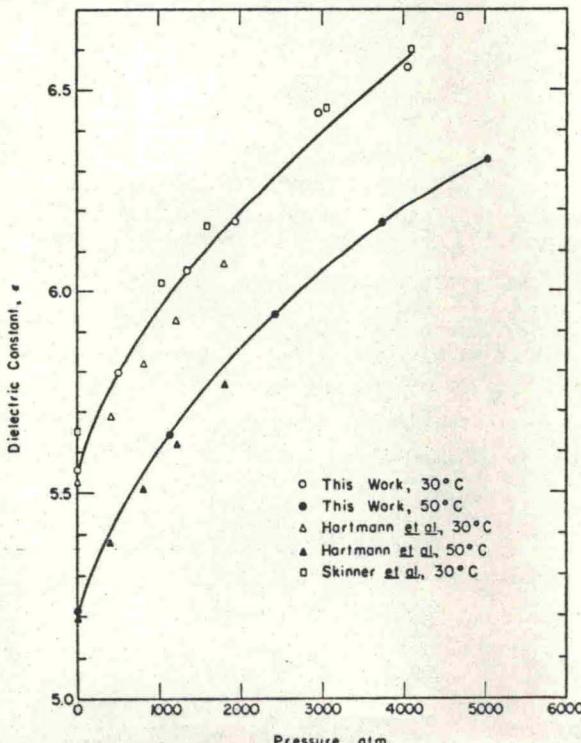


Figure 6. Dielectric constant of chlorobenzene as a function of pressure.

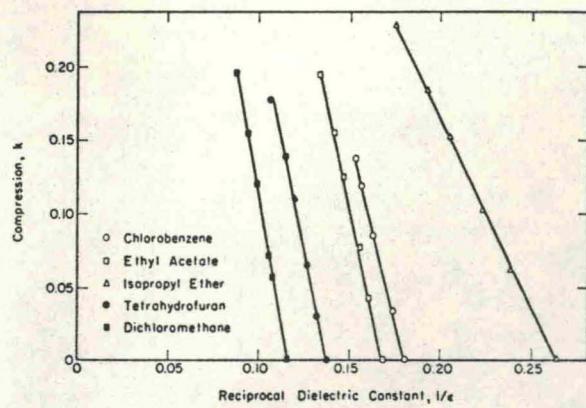


Figure 7. Compression as a function of reciprocal dielectric constant at 30°.

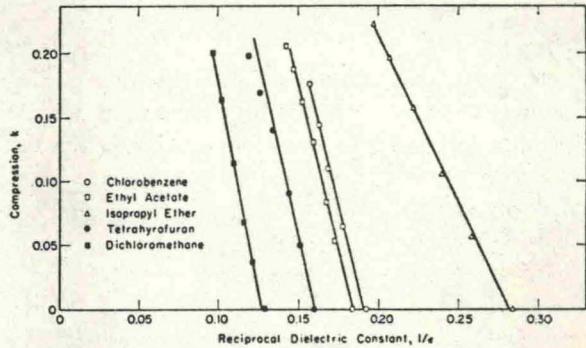


Figure 8. Compression as a function of reciprocal dielectric constant at 50°.

and lie between the two sets. The variation with pressure is quite similar; the major difference seems to be small discrepancies in the dielectric constant at one atmosphere. Also the dielectric constant of dichloromethane at 30° agrees to better than 0.15% with the results of Hartmann and Schmidt<sup>20</sup> up to 600 atm.

In order to check the validity of the assumption of Tait-type expressions to fit both density and dielectric constant with a common parameter  $B$ , plots of the type shown by eq 3 have been constructed (Figures 7 and 8). Except for one case the compression is linear in reciprocal dielectric constant, thus serving as another internal check on the data. The 50° tetrahydrofuran data curve slightly at the higher pressures. After this set of measurements, there appeared to be a small amount of polymer present, and this probably accounts for these deviations. Such an effect has been noted previously.<sup>21</sup>

The density data have been fit to the Tait expression (eq 1) and the dielectric constant to eq 2, 4, and 5. The resulting parameters, along with the average per

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(20) H. Hartmann and A. P. Schmidt, *Ber. Bunsenges. Phys. Chem.*, **72**, 879 (1968).

(21) K. E. Weale and S. A. Mehdi, "Conférence Internationale sur les Hautes Pressions," le Creusot, France, 1965.

**Table II:** Comparison of Experimental Results with Correlating Equations

Solvent	Temp, °C	Density			Dielectric constant							
		C	B <sup>a</sup>	% dev	A	% dev	A'	B'	% dev	A''	B''	% dev
Chlorobenzene	30	0.2604	1705	0.12	0.1332	0.52	0.2035	842	0.40	0.2303	770	0.33
	50	0.2740	1548	0.08	0.1275	0.33	0.2292	984	0.02	0.2593	885	0.01
Ethyl acetate	30	0.2542	1010	0.12	0.1181	0.10	0.2742	1026	0.09	0.3014	925	0.08
	50	0.2676	1015	0.18	0.1276	0.15	0.2894	986	0.12	0.3190	870	0.14
Isopropyl ether	30	0.2352	596	0.09	0.1519	0.14	0.3391	557	0.09	0.3727	428	0.06
	50	0.2852	780	0.30	0.1738	0.89	0.3178	471	0.11	0.3535	352	0.03
Tetrahydrofuran	30	0.2618	1301	0.15	0.1456	0.18	0.3517	1414	0.14	0.3749	1285	0.13
	50	0.2494	959	0.16	0.1310	0.97	0.4993	2279	0.08	0.5246	1992	0.08
Dichloromethane	30	0.2681	1098	0.10	0.1455	0.22	0.3519	1198	0.18	0.3704	1104	0.16
	50	0.2916	1245	0.17	0.1660	0.68	0.2964	773	0.04	0.3165	709	0.05

<sup>a</sup> Units of B, B', and B'' are atmospheres.

cent deviation of the data from the correlating curve are all given in Table II. It should be noted that the exact values of the parameters are not highly significant, in that for the two-parameter equations there are many sets of parameters which will give fits almost as good as those shown. Further, Hartmann *et al.*<sup>9a</sup> have remarked on the sensitivity of the parameters to the number of points used in the fit or even to the particular values of the pressure at which data were taken.

The Tait C has generally been found to be in the range 0.21–0.22 and fairly insensitive to material. The C's here are relatively constant but 0.04–0.05 higher. All density data are fit to 0.3% or better and the average deviation is less than 0.15%.

The one-parameter fit (eq 2) of the dielectric constant data, using the Tait B, is really quite good. The largest average deviation, for tetrahydrofuran at 50°, is still less than 1% and the average for all points is about 0.4%. This result, along with the linearity of the plots in Figures 7 and 8, seems to indicate that except for the most exacting work, a one-parameter equation is sufficient.

When the same expression is used with two adjustable parameters (eq 4), the average fit is improved to 0.13%, and the dielectric susceptibility approach (eq 5) gives an average deviation of 0.11%. In general B'' is lower than B' (or B) and the A'' is higher than A'.

To gain some insight into the effect of structure on the variation of dielectric constant with pressure, in Figure 9 are compared the results for four ethers—ethyl, *n*-propyl, isopropyl, and tetrahydrofuran. The effect of pressure on dielectric constant is least for the cyclic tetrahydrofuran and greatest for the branched isopropyl ether. The two straight chain ethers are intermediate with the effect being greater on the shorter of the two. These structural effects may be contrasted with those for hydrocarbons.<sup>11</sup> For six hydrocarbons—*n*-pentane, *n*-hexane, *n*-octane, cyclopentane, methylcyclohexane, and 2,2-dimethylbutane, the total change in dielectric constant at 4 kbars ranged only from 11 to 16%, with the maximum effect on *n*-pentane and the

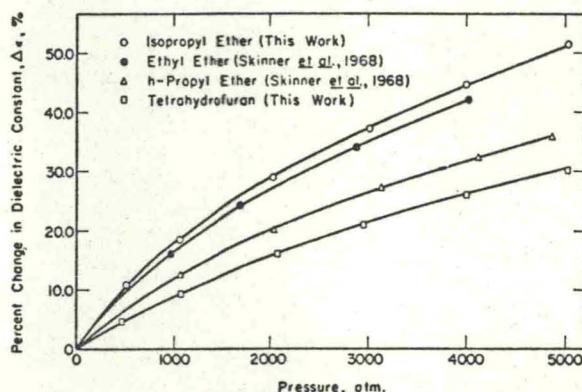


Figure 9. The effect of pressure on the dielectric constant of four ethers at 30°.

minimum for *n*-octane. The cyclic and branched species were intermediate.

### Conclusions

A new technique for the simultaneous determination of the effect of pressure on both density and dielectric constant has been developed and tested. Results are reported for five solvents at two temperatures and at pressures to 5000 atm.

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### Nomenclature

<i>A, B, C</i>	Empirical constants in correlating equations
<i>k</i>	Compression
<i>P</i>	Pressure
<i>v</i>	Molar volume
<i>V</i>	Voltage
<i>ε</i>	Dielectric constant
<i>ρ</i>	Density
Subscripts	
1	At 1 atm
<i>P</i>	At pressure <i>P</i>