SEPTEMBER 15, 1931 PHYSICAL REVIEW VOLUME 38

THE DIELECTRIC CONSTANT OF LIQUIDS UNDER HIGH PRESSURE

By W. E. Danforth, Jr.

Jefferson Physical Laboratory, Harvard University

(Received August 6, 1931)

Abstract

Values of the dielectric constant have been determined for ten liquids at two temperatures and at pressures up to 12,000 atm. except in those cases where freezing would occur at lower pressures. For chloro- and bromobenzene, eugenol, hexyl, isobutyl, and ethyl alcohol, and glycerin, the reciprocal of the Clausius-Mosotti function varies linearly with the density. Carbon disulphide, pentane, and ethyl ether, behave in a somewhat more complicated manner. The linear relations can be explained by variations of the constant of the inner field, the polarizability, or both. A theoretical discussion is given. Anomalous dispersion at 247,000 cycles was observed for eugenol, isobutyl alcohol, and glycerin.

I. Introduction

SEVERAL investigations have been made of the dielectric constant of liquids under pressure and all authors[1–9] agree that the Clausius-Mosotti function decreases. The highest pressures hitherto used were obtained by Kyropoulos[9] who subjected several liquids to pressures up to 3000 kg/cm^2. He showed that the rate of decrease of the function decreases as the pressure increases.

The apparatus available here in Professor Bridgman's laboratory made it possible to extend the investigations in this field over a pressure range four times as great as that of any prior worker. It seemed of interest to determine whether the observations of Kyropoulos would be continued at higher pressures.

Perhaps the most interesting prospect, however, was the effect on the polarization of the viscosity in those liquids where this property increases enormously under pressure. One would expect that the dielectric constant of such liquids would at first rise in the normal manner as pressure was applied. But then when high enough pressures were attained the viscous resistance encountered by the molecules would be so great as to prevent their attaining complete orientation during a half cycle of the alternating field. This phe-

---

[1] Roentgen, Wied. Ann. **52,** 593 (1894).

[2] Ratz, Zeits. Phys. Chem. **36,** 1 (1895).

[3] Ortvay, Ann. d. Physik **36,** 1 (1911).

[4] Falkenberg, Ann. d. Physik **61,** 145 (1920).

[5] Waibel, Ann. d. Physik **72,** 161 (1923).

[6] Grenacher, Ann. d. Physik **77,** 138 (1925).

[7] Francke, Ann. d. Physik **77,** 159 (1925).

[8] Cagniard, Ann. de Physique **9,** 460 (1928).

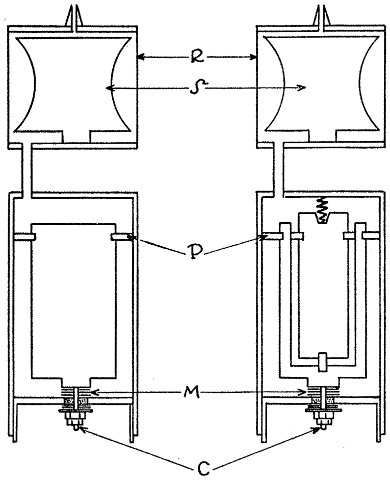
[9] Kyropoulos, Zeits. f. Physik **40,** 507 (1926).

nomenon has been observed in liquids subjected to low temperatures[10–12] and its appearance at high pressures must necessarily follow if the present theoretical view is adequate. In other words, according to the theory, this form of anomalous dispersion is connected in simple manner with the viscosity and should appear when sufficiently high values of this property are produced, irrespective of the means employed.

II. Method

High pressure technique

A hand operated pump was used to produce a pressure of 1000 atmospheres which was transmitted through a glycerin and water mixture to a low-pressure chamber. There it acted upon a large piston which, in turn, pushed a much smaller piston into the high-pressure chamber where petroleum ether was compressed to 12,000 atmospheres.



Figs. 1 and 2. The condensers. *R*, tinfoil reservoir. *P*, glass spacers. *M*, mica insulations. *C*, connection to inner cylinder.

The available motion or "stroke" of the high pressure piston was only a few inches and for compressing the required volume of liquid to 12,000 atmospheres this was inadequate. To circumvent this difficulty an auxiliary press was used which produced a pressure of 2,000 atmospheres in the high pressure chamber before the piston was forced in. This effected a large part of the total required volume reduction, and the subsequent forcing-in of the high-pressure piston produced 12,000 atmospheres without difficulty.

The measurements of pressure were made inside the high-pressure chamber to avoid any uncertainty due to friction of the piston. This was accomplished by measuring the resistance of a coil of manganin wire, a material which is known to have a linear pressure variation.

---

[10] Mizushima, Bull. Chem. Soc. Japan **1**, 47, 83, 115, 143, 163 (1926); Phys. Zeits. **28**, 418 (1927).

[11] Goldammer and Sack, Phys. Zeits. **31**, 225 (1930).

[12] Debye, Polar Molecules, Chemical Catalogue Co.

The measuring condensers

Figs. 1 and 2 show the design of the condensers. At the top of each is a tinfoil reservoir, both condenser and reservoir being filled with the desired liquid and sealed with solder. The whole device is placed in a steel cylinder and pressure applied through petroleum ether. The thin walls of the reservoir permit transmission of the pressure to the liquid within the condenser.

Fig. 1 represents a condenser similar with slight modifications to one used by Chang in an unpublished investigation on this subject. Its capacity was 18.4 mmf. That of Fig. 2 had the larger capacity of 35.4 mmf.

The capacity measurements

Two sets of apparatus were used for measurements of capacity at high and audible frequencies, respectively.

The audible frequency measurements were made on a Nernst bridge using a variable frequency electron tube oscillator as a source of alternating current. The test condenser was in parallel with a General Radio precision condenser in one bridge arm. Upon applicaton of pressure the increase in the capacity of the test condenser was measured by that reduction of the precision condenser necessary to restore balance.

A heterodyne substitution method was used for high frequencies. Two electron tube oscillators with frequencies of about 247,000 cycles gave an audible beat note. The frequency of one was constant and that of the other was controlled by the precision condenser having the test cell in parallel. The precision condenser was adjusted until a beat note of a given frequency was heard. The frequency of the beat note was set by comparing it with that of an audio-frequency oscillator loosely coupled to the telephone circuit. Then when the capacity of the test cell had been changed by the application of pressure the precision condenser was altered until the same beat frequency was heard.

The "air capacity" of the test cell was determined by measuring its capacity before and after filling with a liquid of known dielectric constant. Ethyl ether was used as the calibrating fluid, all determinations being made with samples taken from the same bottle. Its dielectric constant as measured in a specially designed variable condenser was 4.15 at 30°C.

Knowing the air capacity of the test condenser, the dielectric constant of a liquid at atmospheric pressure, and the capacity increase of the condenser filled with liquid when pressure was applied, the dielectric constant at that pressure could be computed.

Two easily determined corrections were necessary. One was due to elastic shortening of the condenser under pressure; the other was an extraneous capacity change introduced through compression of the lead-in insulation.

Preparation of materials

The substances studied were as follows: *Ethyl ether*—Put up by Baker Chemical Co. who had distilled it over sodium, used as received. *Carbon disulphide*—C.P. grade from Mallinckrodt, used as received. *Pentane*—Used as received from Eastman Kodak Company. *Chloro- and bromobenzene*—

Kahlbaum's purest grade, used as received. *Eugenol*—C.P. specimen put up by Merck. It had a light yellow color but no purification was attempted. *Hexyl alcohol*—This was Kahlbaum's purest grade but had a light yellow color. It was refluxed over CaO for several hours and then distilled into the condenser in dry air. The distillate was colorless. *Isobutyl alcohol*—A specimen from Eastman, distilled over CaO in a dry atmosphere. *Ethyl alcohol*—C.P. grade of "absolute" ethyl alcohol, redistilled over CaO in a dry atmosphere. *Glycerin*—C.P. specimen from Mallinckrodt, dehydrated by boiling off one third of its volume at a pressure of 3 cm.

III. Results

The data obtained for the 10 liquids described are set forth in Tables I and II and in Figs. 3–5. The variation of the dielectric constant itself with

TABLE I. *Dielectric constant and Clausius-Mosotti function (P) at high pressures.*

CS_2	p	30°			75°		
		ϵ	ρ	P	ϵ	ρ	P
Carbon	1	2.61	1.241	0.282	—	—	—
disulphide	500	2.74	1.291	.282	—	—	—
	1000	2.82	1.332	.282	2.69	1.286	0.282
	2000	2.94	1.394	.281	2.83	1.357	.281
	4000	3.11	1.487	.277	3.02	1.458	.277
	6000	3.23	1.550	.274	3.16	1.521	.274
	8000	3.33	1.601	.273	3.28	1.575	.273
	12000	3.52	1.689	.271	3.45	1.661	.271
$(C_2H_5)_2O$	1	4.15	.720	.710	—	—	—
Ethyl ether	500	4.53	.771	.710	3.82	.709	.695
	1000	4.88	.801	.710	4.08	.740	.695
	2000	5.39	.847	.707	4.52	.797	.695
	4000	6.05	.911	.700	5.17	.866	.690
	6000	6.53	.952	.690	5.67	.906	.682
	8000	6.93	.988	.676	6.00	.941	.672
	12000	7.68	1.047	.655	6.94	.999	.655
C_5H_{12}	1	1.82	.613	.356	—	—	—
Pentane	500	1.90	.664	.354	—	—	—
	1000	1.96	.701	.352	1.92		
	2000	2.03	.743	.349	2.00		
	4000	2.12	.796	.345	2.11		
	6000	2.19	.835	.342	2.17		
	8000	2.24	.865	.340	2.22		
	12000	2.33	.907	.339	2.31		
C_6H_5Cl	1	5.41	1.004	.592	4.90	.960	.589
Chlorobenzene	500	5.59	1.038	.584	5.12	1.000	.579
	1000	5.75	1.065	.576	5.28	1.030	.571
	2000	5.98	1.105	.566	5.51	1.074	.559
	4000	6.33	1.152	.554	5.88	1.131	.547
	6000	—	—	—	6.12	1.172	.538
	8000	—	—	—	6.29	1.204	.529
C_6H_5Br	1	5.22	1.465	.399	4.87	1.402	.402
Bromobenzene	500	5.36	1.525	.389	5.05	1.461	.393
	1000	5.47	1.558	.384	5.16	1.499	.387
	2000	5.64	1.615	.376	5.34	1.560	.378
	4000	5.88	1.705	.365	5.62	1.648	.367
	6000	—	—	—	5.81	1.716	.359
	8000	—	—	—	5.95	1.762	.354

TABLE I. (*Continued*).

		30°			75°		
$C_6H_{13}OH$	p	ϵ	ρ	P	ϵ	ρ	P
	1	12.90	.812	.984	8.55	.784	.914
Hexyl alcohol	500	13.23	.839	.956	8.97	.812	.892
	1000	13.54	.861	.938	9.32	.837	.877
	2000	14.12	.894	.912	9.83	.874	.855
	4000	15.06	.937	.883	10.42	.921	.826
	6000	—	—	—	10.81	.957	.806
	8000	—	—	—	11.15	.987	.790
		0°			30°		
C_2H_5OH	1	27.8	.806	1.117	23.2	.781	1.127
Ethyl alcohol	500	28.6	.837	1.080	24.5	.816	1.088
	1000	29.4	.864	1.051	25.3	.844	1.057
	2000	30.6	.901	1.008	26.4	.884	1.014
	4000	32.5	.955	.956	28.7	.943	.959
	6000	34.0	.999	.918	30.3	.986	.932
	8000	35.3	1.031	.892	31.7	1.019	.895
	12000	37.6	1.082	.854	33.7	1.073	.857
C_4H_9OH	1	21.1	.819	1.063	17.3	.806	1.056
i-butyl alcohol	500	22.3	.854	1.022	18.1	.832	1.027
	1000	22.9	.877	.998	18.7	.856	1.004
	2000	23.8	.911	.963	19.6	.895	.969
	4000	25.0	.964	.916	20.9	.949	.925
	6000	26.0	1.001	.887	22.0	.989	.893
	8000	26.8	1.031	.864	22.8	1.018	.869
	12000	28.2	1.080	.828	23.9	1.069	.834
$C_3H_5(OH)_3$	1	49.9	1.272	.740	42.8	1.254	.744
Glycerin	500	51.0	1.292	.731	43.9	1.274	.733
	1000	51.9	1.305	.724	44.8	1.287	.728
	2000	53.5	1.330	.711	46.4	1.312	.714
	4000	56.4	1.367	.694	49.1	1.349	.698
	6000	58.9	1.398	.680	51.6	1.380	.684
	8000	61.1	1.429	.666	53.8	1.410	.671
	12000	—	—	—	57.6	1.470	.645
$C_{10}H_{12}O_2$	1	10.49	1.081	.703			
Eugenol	500	10.67	1.105	.693			
	1000	11.04	1.124	.685			
	2000	11.42	1.155	.672			
	3000	11.66	1.177	.663			

TABLE II. *Anomalous dispersion 247,000 cycles.*

Isobutyl Alcohol 0°C		Glycerin 0°C	
p	ϵ	p	ϵ
1	21.13	1	49.9
484	22.34	484	50.9
968	22.90	968	51.9
1940	23.72	1940	53.4
2900	24.38	2940	54.8
3870	24.90	3610	55.5
5810	25.90	4290	55.6
7740	26.70	4960	55.4
9490	27.26	5420	54.9
9680	27.38	6330	52.2
10100	27.30	6710	49.9
10830	27.23	7230	46.6
11290	27.00	7680	44.1
12130	26.35	8490	40.1

TABLE II. (*Continued*).

Eugenol					
0°		30°		50°	
p	ϵ	p	ϵ	p	ϵ
1	10.49	1	9.42	1	8.56
611	10.88	971	9.99	1220	9.28
1240	11.12	2080	10.48	2010	9.57
1785	11.36	2960	10.79	4040	10.20
2370	11.48	4110	11.08	6050	10.67
2550	11.53	5081	11.09	7120	10.70
2670	11.50	5400	10.90	7510	10.62
2780	11.37	5430	10.87	7540	10.49
2920	11.14	5510	10.74	8000	9.66
3030	10.91	5620	10.57	8560	8.20
3280	10.26	5800	10.10		
		6050	9.33		
		6300	6.05		

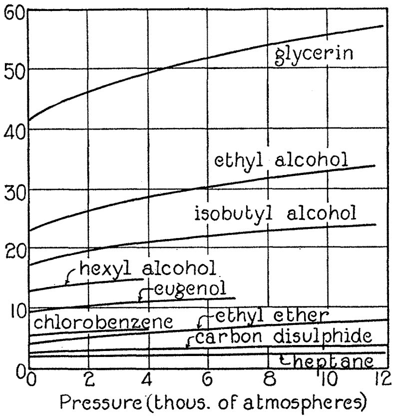


Fig. 3. Variation of dielectric constant at 30° C with pressure.

pressure is presented in Fig. 3. One sees that the curves follow the same trend as was shown in Kyropoulos's data.

The Clausius-Mosotti function (P) also continues the same general sort of variation to 12,000 atm. as was observed by Kyropoulos up to 3,000. But I found that considerable simplification appeared if the reciprocal of the function were plotted against, not the pressure, but the density. No graph of the function itself against pressure is included since I feel that the function has no molecular significance in the case of polar liquids.

Fig. 4 shows the variation of the reciprocal of the Clausius-Mosotti function with density. One observes that for all of the polar liquids except ether the curves are linear. Ether, carbon disulphide, and pentane are more complicated. It is surprising that the liquids supposedly of the more complex internal structure behave in the simpler manner.

The similarity between the slopes of the curves for different liquids is striking. The Clausius-Mosotti function usually shows greater decrease at a given pressure for liquids of higher dielectric constant, but when its reciprocal is plotted against density these differences are largely erased.

It may also be pointed out that the slope of the lower temperature curve is slightly greater in all cases.

In Fig. 5 are shown curves for the three liquids which showed anomalous dispersion at 247,000 cycles under pressure.

IV. Discussion

Since the interpretation of the above presented results is to be from a general point of view, it will be well to review briefly the fundamentals of the subject.

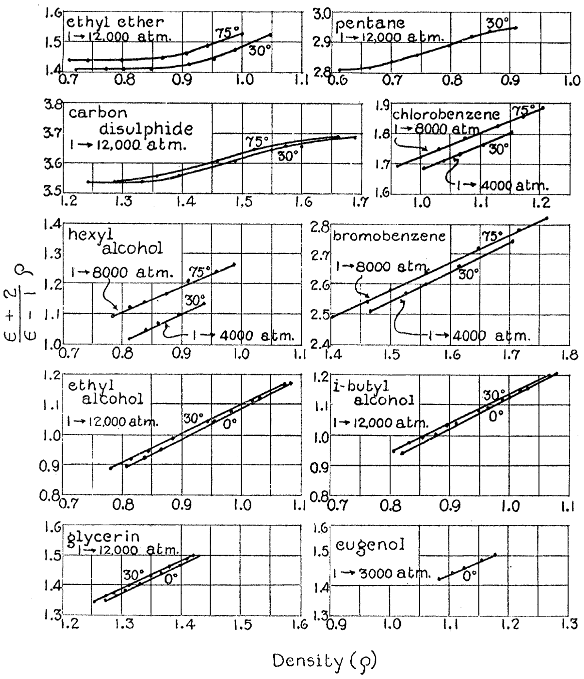


Fig. 4. Reciprocal of Clausius-Mosotti functions at high pressures.

Outline of theory

The outstanding characteristic of dielectric behavior is the direct proportionality between the dielectric polarization and the applied field. This enables one to describe the behavior of a given substance under given physical conditions by means of a single number called the dielectric constant.

In the formulation of a molecular theory for the dielectric constant expressions must be found for three fundamental processes:

(a). The way in which the applied field is modified to give the force acting on an individual molecule.

(b). The relation between this "inner force" and the moment induced in the individual molecule.

(c). The way in which the induced molecular moments combine to give the observed large-scale polarization.

It is perhaps trivial to mention item (c). The polarization per unit volume (I) of the material is simply the number of molecules per unit volume (n) times the induced electric moment (m) of each,

$$\text{i.e.,}\ I = nm \tag{1}$$

In the expression of items (a) and (b) one may make use of the observed proportionality between the polarization and the applied field. The polarization is produced by the action of the inner field on the molecules, and the inner field is itself a function both of the applied field and of the polarization.

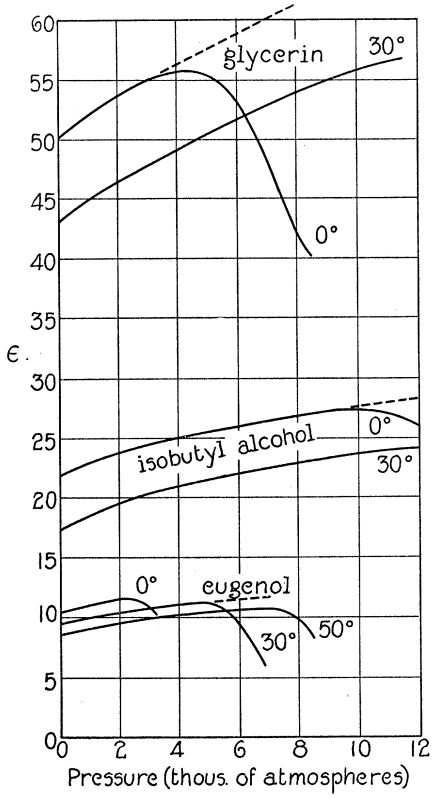


Fig. 5. Anomalous dispersion in liquids at high pressures. Solid lines, 247,000∽. Dotted lines 3,710∽.

The simplest way to describe this situation is to assume that the induced moment of a molecule is directly proportional to the inner force and that the latter is a linear function of the applied field and the polarization. One realizes, however, that linearity in both of these relations is not necessary. Deviations from linearity in the induced moment may be compensated for by oppositely-sensed deviations in the expression for the inner field, and the proportionality between polarization and the applied field may still obtain.

That such mutual compensation should exist in all of the many varieties of materials seems rather improbable. And further, modern atomic theory looks with entire satisfaction on the notion of a linear polarizability. Hence it seems safe to assume linearity in both of these relations. One says that the induced moment (m) may be written:—

$$m = \alpha F \tag{2}$$

where α is a constant polarizability, and one writes for the inner field:

$$F = E + \nu I \tag{3}$$

where ν is the "constant of the inner field" and determines the extent to which the applied field is modified by the polarization (I).

Now from the equations of elementary electrostatics one can obtain the following quite general relation:

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{\rho} = \frac{4\pi N\alpha}{3 + (4\pi - 3\nu)N\alpha\rho} \tag{4}$$

where ϵ is the dielectric constant, ρ the density, and N the number of molecules per unit mass.

This expression involves no assumptions regarding the inner field except that it varies linearly with the polarization. Its left hand side is the familiar Clausius-Mosotti function. In the usual theory the force on a molecule is assumed to be the same as if the latter were at the center of a spherical cavity in the material. One could then write $\nu = 4\pi/3$ and the above equation would reduce to:

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{\rho} = \frac{4\pi}{3} N\alpha.$$

If this is true it is seen that the expression $\epsilon - 1/(\epsilon + 2)\rho$ (which will hereinafter be denoted by P) is a measure of the molecular polarizability of the material. But in the case of liquids the assumption that $\nu = 4\pi/3$ is highly questionable so in general the function P has no simple molecular significance.

Interpretation of results

In a preceding section of this paper it was found that the simplest way to present the pressure variation of the dielectric constant is to plot the reciprocal of the Clausius-Mosotti function against the density.

When this is done the liquids of higher dielectric constant (chloro- and bromobenzene, hexyl, isobutyl, and ethyl alcohol, eugenol, and glycerin) give straight lines. Ether starts out horizontally and curves upward rather abruptly at about 4,000 atm. after which it seems to be fairly linear. Carbon disulphide and pentane, two nonpolar liquids, seem to start out horizontally, curve upwards, and then flatten out again at high pressures.

The decrease of the Clausius-Mosotti function P does not necessarily indicate a diminished polarizability. The above outlined theory gives us two theoretical quantities (ν and α) which may vary and account for the observations. But it may be mentioned that the decrease with increasing density may take place without either of these quantities varying. With a constant polarizability, P will increase under pressure if ν is greater than $4\pi/3$ and decrease if it is less.

This can be seen at once if one writes the reciprocal of Eq. (4).

$$1/P = 3/4\pi N\alpha + (1 - 3\nu/4\pi)\rho. \tag{5}$$

But it also follows that α should be given by the intercept at $\rho = 0$, according to the relation,

$$1/P_0 = 3/4\pi N\alpha \tag{6}$$

and values so calculated are much larger than those measured in dilute solutions. It seems certain, therefore, that either α or ν, or both, must vary as the pressure is applied.

Unfortunately we haven't enough machinery to handle the situation if both are considered as variables. So the best we can do is to consider separately the two cases in which one is allowed to vary and the other is held constant.

(1). Let us first assume that the constant of the inner field ν is independent of the density and that the polarizability α varies. Inspection of Eq. (5) shows that the linear curves may be thus described if α follows the relation:

$$1/\alpha = 1/\alpha_0 + A\rho. \tag{7}$$

It may also be seen that A and ν, and the observed slope (m) are connected by the equation:

$$\nu = 4\pi(1 - m + A/N)/3. \tag{8}$$

This, of course, is of no value unless the constant A can be determined in some way. Knowledge of ν would permit this by means of Eq. (8), or if α were known at some value of ρ, Eq. (7) could be used. A theoretical deduction of either of these quantities would permit the evaluation of the other. But at present there seems no way out of the difficulty.

It seems highly improbable that in the case of polar liquids one can assume that $\nu = 4\pi/3$. The simplicity which this assumption lends to the equations, however, has led to its provisional acceptance in many doubtful cases. So an interpretation on this basis will not be without precedent. If this assumption is made, α can be computed directly from P. In the case of ether, α apparently decreases markedly but the difference between the curves at different temperatures seems to increase. This would mean an increasing permanent moment but a decreasing polarizability, which is inconsistent. It is also difficult to see why the value of α for the nonpolar liquids should decrease much under pressure. But the liquids whose curves are linear seem more consistent. The curves for the two temperatures seem to converge, and the decrease of the permanent moment (due to compression of the molecules or to association) calculated therefrom, is of the right order of magnitude to account for the decrease of P. The data are not accurate enough to verify this exactly.

(2). The alternative interpretation consists in assuming that the polarizability remains constant and that the constant of the inner field varies with the density. In some ways this seems to be the more logical method. The quantity ν is determined by the mutual arrangement of the molecules and hence seems more likely to depend on the density than does α which is more of an intrinsic molecular property.

If therefore, we let α be constant (e.g. the same as that of a molecule in dilute solution) we find that, in order to explain the observed linear curves we must let ν vary according to the relation:

$$\nu = 4\pi(1 - m)/3 + K/\rho \tag{9}$$

and it is at once apparent that since α is known and is independent of density, K can be evaluated from the intercept relation:

$$1/P_0 = 3/4\pi N\alpha - 3/4\pi K. \tag{10}$$

Data are at hand for the polarizabilities of only two of the liquids which give linear curves. Calculations carried through for these two lead to the results:

For ethyl alcohol $\nu = 0.196 + 2.07/\rho$
For chlorobenzene $\nu = 0.853 + 1.99/\rho$

It may be noted that the more highly polar of the two, ethyl alcohol, has the stronger density dependence. This is perhaps to be expected since larger permanent moment means stronger intermolecular forces and hence lends more importance to the mean distance between molecules.

Some readers might object to this interpretation on the grounds that it neglects the hypothesis of molecular association. I would point out however, that association was first brought in as a device to cover up discrepancies arising from the assumption that $\nu = 4\pi/3$. Its first application in dielectric theory was as a means of explaining the results of binary mixture experiments. The $\nu = 4\pi/3$ assumption lent a beautiful simplicity to the equations, and the association hypothesis possessed a pleasing concreteness. But it must be remembered that the observations might also have been described, and the doubtful assumption avoided, by allowing ν to vary instead of α. This is not to say that association does not exist. The rigid pairing of molecules is a logical mechansim to explain changes of α with concentration or with pressure. But such changes are always masked by variations of ν and nothing definite can be said of either until means are available to study one alone.

Anomalous dispersion at high pressures

Fig. 5 gives curves for the dielectric constant of three liquids, glycerin, isobutyl alcohol, and eugenol, measured at 247,000 cycles. Bridgman's measurements show that the viscosities of these liquids increase under pressure by an unusually large factor. They were therefore chosen as being the most promising materials for observations of anomalous dispersion.

The normal pressure effect is of course an increase in the dielectric constant. The curves rise as pressure is applied until a point is reached where the molecular orientation begins to be suppressed by the viscous resistance. At this point the curves pass through maxima and thereafter decrease. The dotted curves show measurements at an audible frequency. The fact that they show no unusual variation proves the important point that the observed maxima are not due to freezing.

Debye's theory of anomalous dispersion in liquids[12] assumes $4\pi/3$ as the constant of the inner field and hence cannot be expected to apply to these highly polar liquids. Calculations of the molecular radii using Bridgman's viscosity data gave values considerably too small and decreasing rapidly as the viscosity was increased.

ACKNOWLEDGMENT

Without Professor P. W. Bridgman's extensive experience in high pressure research this investigation would have been quite impossible. I wish to express my thanks for his stimulating interest. I am also indebted to the Cruft Laboratory of this University for the loan of electrical apparatus.