The Effect of Pressure upon the Dielectric Constants of Liquids

Benton Brooks Owen, *Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut*

AND

Stuart R. Brinkley, Jr.,* *Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts***

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An empirical equation containing two parameters A and B is shown to express the isothermal variation of the dielectric constants of liquids with pressure. The equation is analogous to the Tait equation for the variation of the densities of liquids with pressure. The parameter B is common to both equations, and therefore may be determined independently from either dielectric constants or densities. Furthermore B can be eliminated between the two equations to give a linear relationship between the reciprocals of the dielectric constant and the density. It is shown that this linear relationship may be derived from Tammann's hypothesis and electrostatic theory.

(1) INTRODUCTION

AN accurate knowledge of the pressure dependence of the dielectric constants (D) of various solvents is of great importance in the study of certain partial molal properties of electrolytes in solution.[1] Good values of D and $\partial(1/D)/\partial P$ will suffice for the study of partial molal volumes, but $\partial^2(1/D)/\partial P^2$ and $\partial^2(1/D)/\partial P\partial T$ are required for partial molal compressibilities and expansibilities. Since dielectric constant measurements at high pressures are usually less precise than those at one atmosphere, the second derivatives cannot be satisfactorily evaluated unless the proper functional relationship between D and P is known. It is our purpose to show that this relationship takes the simple form[2]

$$1-\frac{D^{(1)}}{D^{(P)}}=AD^{(1)}\log\frac{B+P}{B+1} \tag{1}$$

for pressures up to several thousand atmospheres and appears to be completely analogous to the Tait[3] equation

$$1-\frac{\rho^{(1)}}{\rho^{(P)}}=C\rho^{(1)}\log\frac{B+P}{B+1} \tag{2}$$

written in terms of the density, ρ.

* National Research Fellow in Chemistry.
** Present address, Department of Chemistry, Cornell University, Ithaca, New York.
[1] F. T. Gucker, Jr., Chem. Rev. **13**, 111 (1933).
[2] The pressure at which a quantity is measured is indicated in parenthesis as a superscript.
[3] P. G. Tait, "Report on some of the physical properties of fresh water and sea water," *Physics and Chemistry of the Voyage of H.M.S. Challenger*, Vol. II, Part IV, S.P., LXI (1888).

The parameters of these equations, A, B, and C, are independent of the pressure. B is a function of the temperature, usually decreasing with increasing T. Gibson[4] has shown that Eq. (2) accurately represents the available data up to 10,000 atmospheres and that the product $C\rho^{(1)}$ is independent of the temperature. The results given in the next section indicate that $AD^{(1)}$ is also independent of T, but the evidence is not conclusive. If further measurements verify the temperature independence of $AD^{(1)}$, the analogy between Eqs. (1) and (2) would be complete. This point has practical as well as theoretical interest, for if A can be evaluated at any one temperature from dielectric constants under pressure, the derivatives

$$\left(\frac{\partial(1/D)}{\partial P}\right)^{(P)}=-\frac{0.4343A}{B+P}, \tag{3}$$

$$\left(\frac{\partial^2(1/D)}{\partial P^2}\right)^{(P)}=\frac{0.4343A}{(B+P)^2}, \tag{4}$$

$$\left(\frac{\partial^2(1/D)}{\partial P\partial T}\right)^{(P)}=\frac{0.4343A}{(B+P)^2}\left(\frac{\partial B}{\partial T}\right)$$
$$+\frac{0.4343A}{D^{(1)}(B+P)}\left(\frac{\partial D}{\partial T}\right)^{(1)} \tag{5}$$

could be evaluated at any temperature at which $D^{(1)}$ and B are known as functions of T. The fact that B can be conveniently determined from

[4] R. E. Gibson, J. Am. Chem. Soc. **56**, 4 (1934); *ibid.*, **57**, 284 (1935). See also A. Wohl, Zeits. f. physik. Chemie **99**, 234 (1921), and H. Carl, *ibid.* **101**, 238 (1922).

TABLE I. Comparison of Eq. (1) with experimental data.

Liquid	$t°$	#	P_{max}	$D^{(1)}$	$AD^{(1)}$	B^a	Δ_{Av}	Δ_{max}
			Data of Kyropoulos					
Water	20	7	3000	80.79	0.4060	2963*	0.06	0.15
Methanol	20	7	3000	33.79	.2905	1187	.07	.16
Ethanol	20	7	3000	25.71	.2663	1255	.08	.23
Acetone	20	7	3000	21.50	.2577	784	.08	.19
Pyridine	15	11	2500	13.93	.3504	1667	.05	.18
Chloroform	18.5	7	3000	4.955	.2478	916	.05	.23
Ethyl ether	20	7	3000	4.328	.3707	588	.09	.17
Carbon disulfide	20	7	3000	2.647	.2516	1275	.12	.26
Benzene	18	3	400	2.288	.1327^b	1021*	.10	.30
Carbon tetrachloride	18	5	1000	2.246	.1581^b	916*	.23	.55
Petroleum ether	18.4	7	3000	1.870	.1398	588	.06	.10
			Data of Danforth					
Glycerol	0	7	8000	49.9	0.3708	3838	0.08	0.16
Glycerol	30	8	12000	42.8	.4032	3664	.11	.28
Ethanol	0	8	12000	(27.7)	.3030	1884	.19	.54
Ethanol	30	8	12000	(23.3)	.3048	1290	.34	.83
i-Butanol	0	8	12000	(21.7)	.2469	1623	.48	2.75
i-Butanol	30	8	12000	17.3	.2521	1034	.19	.36
Hexanol	30	5	4000	12.90	.4210	3391	.04	.08
Hexanol	75	7	8000	8.55	.2197	742	.25	.63
Eugenol	30	5	3000	10.49	.2544	1967	.39	.84
Chlorobenzene	30	5	4000	5.41	.2240	1210*	.10	.28
Chlorobenzene	75	7	8000	4.90	.2219	897*	.15	.34
Bromobenzene	30	5	4000	5.22	.1880	1364*	.02	.04
Bromobenzene	75	7	8000	4.87	.1923	1036*	.12	.26
Ethyl ether	30	8	12000	4.15	.3506	608	.50	.93
Ethyl ether	75	7	12000	(3.39)	.3612	507	.64	1.67
Carbon disulfide	30	8	12000	(2.63)	.2203	1013	.20	.85
Carbon disulfide	75	6	12000^c	(2.47)	.2428	871	.05	.29
Pentane	30	8	12000	1.82	.1729	709	.06	.53
Pentane	75	6	12000^c	(1.78)	.1726	608	.08	.47
			Data of Francke					
Benzene	18	14	700^d	(2.2709)	0.1327	1021*	0.03	0.07
Carbon tetrachloride	18	16	800^d	(2.2220)	.1581	916*	.02	.04
Heptane	18	16	800^d	(1.9400)	.1118	608	.02	.06
Hexane	18	16	800^d	(1.8220)	.1299	658	.02	.05

Values in parenthesis extrapolated from results at higher pressures.
Number of pressures at which D was measured.
P_{max} Upper limit of experimental pressure range. Lower limit 1 atmos. unless otherwise noted.
Δ_{Av} and Δ_{max} percent difference between $D^{(P)}$ observed and calculated by Eq. (1).
* Values of B derived from compressibility data of Gibson.
^{a} All values of B have been converted to bars for consistency in tabulation, although some of the data were expressed in atmospheres and some in kg per cm².
^{b} From Francke's data below.
^{c} Lower pressure limit 1000 atmos.
^{d} Lower pressure limit 50 atmos.

density (compressibility) data extends the range of such calculations enormously, for very little work has been done on dielectric constants under pressure at more than one temperature.

Another important feature of Eqs. (1) and (2) is that elimination of the common term yields the linear relationship

$$1 - \frac{D^{(1)}}{D^{(P)}} = \frac{AD^{(1)}}{C\rho^{(1)}}\left(1 - \frac{\rho^{(1)}}{\rho^{(P)}}\right) \quad (6)$$

between the reciprocals of the dielectric constant and the density. In Section (3) it will be shown that this simple relationship can be derived from

Tammann's hypothesis and electrostatic theory. The analogy between the two empirical Eqs. (1) and (2) is therefore not fortuitous because either one may be derived from the other with the aid of Eq. (6).

(2) VERIFICATION OF THE EQUATIONS BY COMPARISON WITH EXPERIMENTAL RESULTS

Table I contains the results of fitting Eq. (1) to the experimental data of Kyropoulos,[5] Danforth,[6] and Francke.[7] The parameters were

[5] S. Kyropoulos, Zeits. f. Physik 40, 507 (1926).
[6] W. E. Danforth, Jr., Phys. Rev. 38, 1224 (1931).
[7] C. Francke, Ann. d. Physik 77, 159 (1925).

TABLE II. Re-evaluation of the parameters of Eq. (1) keeping $AD^{(1)}$ independent of the temperature.

Liquid	$t°$	$D^{(1)}$	$AD^{(1)}$	B	Δ_{Av}	Δ_{max}	Data
Glycerol	0	49.9	0.3870	4090	0.07	0.21	Danforth
Glycerol	30	42.8	.3870	3424	.14	.32	Danforth
Ethanol	0	(27.7)	.3039	1884	.32	.62	Danforth
Ethanol	20	25.71	.3039	1452	.24	.88	Kyropoulos
Ethanol	30	(23.3)	.3039	1290	.36	.79	Danforth
i-Butanol	0	(21.7)	.2495	1644	.49	2.75	Danforth
i-Butanol	30	17.3	.2495	1023	.18	.53	Danforth
Hexanol	30	12.90	.2200^a	1309	.54	1.06	Danforth
Hexanol	75	8.55	.2200^a	752	.25	.63	Danforth
Chlorobenzene	30	5.41	.2230	1210*	.11	.35	Danforth
Chlorobenzene	75	4.90	.2230	897*	.15	.40	Danforth
Bromobenzene	30	5.22	.1902	1364*	.06	.19	Danforth
Bromobenzene	75	4.87	.1902	1036*	.17	.33	Danforth
Ethyl ether	20	4.328	.3559	541	.07	.31	Kyropoulos
Ethyl ether	30	4.15	.3559	630	.55	1.11	Danforth
Ethyl ether	75	(3.39)	.3559	497	.71	2.30	Danforth
Carbon disulfide	20	2.647	.2316	1133	.16	.30	Kyropoulos
Carbon disulfide	30	(2.63)	.2316	1100	.30	.77	Danforth
Carbon disulfide	75	(2.47)	.2316	776	.20	.26	Danforth
Petane	30	1.82	.1728	709	.06	.53	Danforth
Petane	75	1.78	.1728	608	.08	.47	Danforth

* Values of B derived from compressibility data of Gibson.
^{a} In this case the average value of $AD^{(1)}$ was not used. The value at 75° was chosen as being more in line with the general trend for the alcohols. This choice gives a more "reasonable" value of B at 30°, but increases the deviations considerably.

evaluated by the method of least squares. In this procedure, infinite weight was given to the value of $D^{(1)}$ except for those liquids for which $D^{(1)}$ was not recorded,[8] or was clearly inconsistent with the results at higher pressures.[9] In these exceptional cases $D^{(1)}$ was treated as a third empirical parameter and evaluated accordingly. Whenever B could be obtained from Gibson's[10] compressibility data, this value was used, and only A had to be evaluated from the measurements of $D^{(P)}$. This simultaneous use of Eqs. (1) and (2) is equivalent to the use of Eq. (6), so no separate verification of the latter equation will be given.[11]

The average and maximum differences (percent) between observed values of $D^{(P)}$ and those calculated by Eq. (1) are given in the last two columns of Table I. With only two exceptions,[12]

[8] Danforth's data for carbon disulfide (75°), pentane (75°), and the data of Francke.
[9] Danforth's ethanol (0 and 30°), i-butanol (0°), ethyl ether (75°), and carbon disulfide (30°).
[10] Values of B for a number of solvents at 25 to 85° were kindly supplied by Dr. R. E. Gibson of the Geophysical Laboratory, Washington, D. C. For purposes of interpolation and extrapolation, we fitted these values to cubic equations in $(t-25)$ by the method of least squares.
[11] The values of $D^{(P)}$ and $\rho^{(P)}$ recorded by Danforth are unsuitable for a direct test of Eq. (6) because the data are not given to a sufficient number of significant figures, and are not always consistent with the accepted values of $D^{(1)}$ and $\rho^{(1)}$.
[12] It is not unreasonable to attribute these unusually large differences to experimental errors. Thus, one of the

these differences show that the equation will represent the data to within a few units in the last significant figure in $D^{(P)}$. This is very good agreement indeed, considering the wide range in D and P covered by the experiments and the fact that in one-third of the comparisons B was calculated from compressibility data. Furthermore, in comparing the equation with Kyropoulos' data for benzene and carbon tetrachloride, both A and B were derived from other sources.

Table I also shows that the values of $AD^{(1)}$ obtained from Danforth's data are insensitive to the temperature, particularly if an accurate value of B from compressibilities is employed. In order to investigate this point, we have averaged the values of $AD^{(1)}$ from Danforth's data in Table I and re-evaluated B. The results are given in Table II, where it can be seen that the assumption of the temperature independence of $AD^{(1)}$ has very little effect upon the concordance between Eq. (1) and experiment. The means of the values of Δ_{Av} and Δ_{max} in Table II are 0.24 and 0.72, while the means of the corresponding values in Table I are only slightly less, viz., 0.20 and 0.58. Only in the case of ethanol at 20° were

eight experimental points on the curve for i-butanol at 0° is quite out of line, and if this point is neglected the differences are reduced to 0.15 and 0.25. Ethyl ether at 75° might easily yield erroneous results if contaminated by certain impurities.

systematic departures from the equation caused by keeping $AD^{(1)}$ independent of temperature.

There is one other verification of Eq. (1) which is worthy of note. Since the dielectric constant of a liquid of unit permeability is equal to the square of the index of refractions, we can write Eq. (1) in the form

$$1 - \frac{n^{2\,(1)}}{n^{2\,(P)}} = A n^{2\,(1)} \log \frac{B+P}{B+1} \qquad (7)$$

for such liquids. Table III shows the results of fitting this equation to the data of Gibson and Kincaid[13] for benzene, a liquid for which the permeability is very close to unity. The ability of the equation to represent the data with high precision is remarkable, particularly because B was determined from compressibilities, and only the one parameter, A, was adjusted to fit the index of refraction data. This constitutes a very good indication of the validity of Eq. (6). Furthermore, $A n^{2\,(1)}$ is practically independent of the temperature and may be made absolutely independent of T without seriously increasing the differences between the equation and experiment.

(3) THEORETICAL

The derivation of Eq. (6) involves the calculation of the electrostatic contribution, $V_e^{(P)}$, to the partial molal volume of an electrolyte at infinite dilution by two independent methods. In both calculations $V_e^{(P)}$ is necessarily a function of the radii and other characteristics of the individual ions, but $\partial \log V_e^{(P)}/\partial P$ can be made independent of these characteristics if they are properly chosen. Equation (6) then follows by equating the two expressions for $\partial \log V_e^{(P)}/\partial P$. Since the resulting equation involves only properties of the pure solvent (D and ρ), it should be independent of the characteristics of the ions which were arbitrarily introduced in its derivation. If this be true, the validity of our derivation of the equation depends primarily upon the possibility of endowing a hypothetical electrolyte with properties which simultaneously fulfill all the conditions subsumed in the two independent calculations of $\partial \log V_e^{(P)}/\partial P$.

With these conditions in mind, we will con-

sider a hypothetical electrolyte which dissociates completely into two spherical ions of equal radii (b) supporting equal charges ($\pm z\epsilon$) uniformly distributed upon their surfaces. The ions are incompressible, are very large compared to the solvent molecules, and would behave as ideal solutes in the absence of their charges.

According to Tammann[14] the contraction in volume and decrease in compressibility which accompanies the addition of an electrolyte to a solvent can be ascribed to a compression of the solvent, rather than to any alteration in the solute (other than melting). The pressure increment, P_e, which would be required to produce this compression of the solvent is called the "effective pressure." P_e is a function of the concentration and the properties of the ions and the solvent, but is assumed independent of the external pressure, P, upon the solution. The effective pressure has been very useful in interpreting the behavior of electrolytic solutions, and Gibson[4] has shown that its introduction into the Tait Eq. (2) permits a quantitative representation of the densities and compressibilities of such solutions within the experimental errors.

Since Tammann's hypothesis represents the behavior of real ionic solutions to a close approximation, it should very satisfactorily describe a solution containing our hypothetical incompressible ions. Accordingly we write

$$V^{(P)} = m V_2 + 1000 v^{(P+P_e)} \qquad (8)$$

for the total volume of the solution in terms of the ideal molal volume of the solute, V_2, and the specific volume of the pure solvent, v. Note that

TABLE III. Comparison of Eq. (7) with experimental data for the index of refraction of benzene

λ^a	t°	#	P_{max}	$n^{(1)}$	$A n^{2(1)}$	B	Δ_{Av}	Δ_{max}
589	25	4	868	1.4983	0.1569	970*	0.008	0.019
589	35	4	1030	1.4918	.1564	899*	.014	.026
589	45	4	1188	1.4851	.1562	829*	.016	.029
436	25	4	561	1.5201	.1608	970*	.006	.016
436	35	4	713	1.5134	.1587	899*	.011	.021
436	45	4	867	1.5065	.1582	829*	.008	.020

* Values of B derived from compressibility data of Gibson.
^{a} Wave-length of the light used (mμ).

[13] R. E. Gibson and J. F. Kincaid, J. Am. Chem. Soc. **60**, 511 (1938).

[14] G. Tammann, *Über die Beziehungen zwischen den innern Kräften und Eigenschaften der Lösungen* (Voss, Liepzig, 1907), p. 36.

the apparent volume of the solvent in the solution under the pressure P is represented by the volume of the same quantity of pure solvent under a pressure $P+P_e$. In dilute solutions of large ions, P_e is small, and Eq. (8) may be written

$$V^{(P)} - m V_2 = 1000 v^{(P)} + 1000 (\partial v/\partial P)^{(P)} P_e \quad (9)$$

and, since the partial molal volume, $\bar{V}_2$, is defined as $(\partial V/\partial m)_{T,P}$, we obtain

$$\bar{V}_2^{(P)} - V_2 = 1000 (\partial v/\partial P)^{(P)} (\partial P_e/\partial m). \quad (10)$$

At infinite dilution the left-hand member of this equation is $\bar{V}^\circ_2{}^{(P)} - V_2$. The term $\bar{V}^\circ_2{}^{(P)}$ includes the effect of electrostriction of the solvent, and V_2 is the ideal molal volume of the ions in the absence of electrostriction. The difference between these two volumes is therefore the quantity V_e. Consequently

$$V_e^{(P)} = \bar{V}^\circ_2{}^{(P)} - V_2$$

$$= 1000 (\partial v/\partial P)^{(P)} (\partial P_e/\partial m)_{m=0} \quad (11)$$

and

$$\frac{\partial \log V_e^{(P)}}{\partial P} = (\partial^2 v/\partial P^2)^{(P)}/(\partial v/\partial P)^{(P)} \quad (12)$$

is the result obtained from Tammann's hypothesis.

From consideration of the reversible electrical work (per mole) of charging the ions of an electrolyte at infinite dilution, the electrostatic contribution to the partial molal free energy[15] of the electrolyte is found to be

$$\bar{F}^\circ_2 - F_2 = z^2 \epsilon^2 N/b D^{(P)}, \quad (13)$$

when the cations and anions have equal radii and

[15] G. Scatchard, Chem. Rev. **3**, 383 (1927); J. Chem. Phys. **9**, 34 (1941).

charges. Although the electrical work is most simply calculated[16] by assuming that the ions are uniformly charged spheres in a homogeneous medium of dielectric constant D, alternative calculations[17] which consider the inhomogeneity of the solvent lead to essentially the same result for very large ions. The properties assigned to our hypothetical electrolyte not only fulfill the conditions underlying Eq. (13), but also require the derivative* of this expression to take the simple form

$$V_e^{(P)} = \bar{V}^\circ_2{}^{(P)} - V_2 = \left(\frac{z^2 \epsilon^2 N}{b}\right)\left(\frac{\partial (1/D)}{\partial P}\right)^{(P)}, \quad (14)$$

because the radii of incompressible ions are independent of the pressure.

Logarithmic differentiation of Eq. (14) yields

$$\left(\frac{\partial \log V_e}{\partial P}\right)^{(P)} = \left(\frac{\partial^2 (1/D)}{\partial P^2}\right)^{(P)} \bigg/ \left(\frac{\partial (1/D)}{\partial P}\right)^{(P)} \quad (15)$$

for the electrostatic calculation of the same quantity given by Eq. (12), from Tammann's hypothesis. Combination of Eqs. (12) and (15) gives the differential equation

$$\left(\frac{\partial^2 (1/D)}{\partial P^2}\right)^{(P)} \bigg/ \left(\frac{\partial (1/D)}{\partial P}\right)^{(P)}$$

$$= \left(\frac{\partial^2 v}{\partial P^2}\right)^{(P)} \bigg/ \left(\frac{\partial v}{\partial P}\right)^{(P)} \quad (16)$$

from which Eq. (6) is obtained by integration.

[16] M. Born, Zeits. f. Physik **1**, 45 (1920); E. Guntelberg, Zeits. f. physik. Chemie **123**, 199 (1926).

[17] P. Debye and J. McAulay, Physik. Zeits. **26**, 22 (1925); P. Debye, Zeits. f. physik. Chemie **130**, 56 (1927); J. A. V. Butler, J. Phys. Chem. **33**, 1015 (1929); H. S. Harned and N. N. T. Samaras, J. Am. Chem. Soc. **54**, 9 (1932).
* $(\partial F/\partial P)_T = V$.