

**Dielectric Constant of Liquids (Fluids) Shown to be
Simple Fundamental Relation of Density over Extreme
Ranges from -50° to $+600^{\circ}\text{C}$, Believed Universal**

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ABSTRACT

Examinations of past complex theoretical equations describing isothermal dielectric constants (ϵ) of liquids show that *none* describe experiments throughout and that only a two-constant equation of density is required. The dielectric susceptibility ($\epsilon - 1$) as a simple exponential function of density is shown here to describe ϵ for both polar and non-polar organic liquids over all available experimental ranges from 0.50 to 1.2 g cm^{-3} and temperatures to 400°C . For water above 0.25 g cm^{-3} , the equation describes the excellent dielectric-constant formulation of Fernández, et al., (1997) throughout its experimental range [-35 to 600°C ; to 1000 MPa (10000 Atm)] and even when diluted by "inert" solvents (Marshall, 2008). At lower densities at all temperatures, water susceptibilities converge to an even more simple unit proportionality to density below 0.003 g cm^{-3} , not yet verified for organics without experiment. While the past Born, Tait, Clausius-Mossotti, and Owen-Brinkley theories describe ϵ equally well over a limited 10% change in density, all are shown to fail over greater ranges. The simple density relation presented here should be useful in clarifying and reducing complexity of theory applied to liquid structure.

I. INTRODUCTION

The dielectric constant (ϵ) is an important fundamental property of liquids related to substance polarity and other properties and for evaluations by theory. Scientific interest in this property began in the late 1800's. The dielectric constant is defined as the ratio of electrical capacitance of a substance contained in a given volume, generally a cube, to the equivalent cell capacitance of a vacuum. Thus ϵ increases from unity to higher values as substance density increases from zero. The first measurements of dielectric constant as a function of pressure (density) were those of Roentgen¹ (1894) for water and ethanol that showed less than 1% change in ϵ for these two liquids to 50 MPa at ambient temperature, which was confirmed shortly after by Ratz² who also measured other organics. Even earlier the Clausius-Mossotti function was presented to describe theoretically the polarity of liquids, and many references to this and other early publications on ϵ are given by Danforth.³ In 1913 Bridgman⁴ presented dielectric constant measurements at high pressures for diethyl ether.

Notable publications presenting generally high quality values of dielectric constants for numerous organic and inorganic liquids at temperatures below 100°C at high pressures are those of Danforth³ (carbon disulfide, diethyl ether, n-pentane, chlorobenzene, bromobenzene, hexyl alcohol, ethyl alcohol, iso-butyl alcohol, eugenol - to 1200 MPa), Chang⁵ (toluene, carbon disulfide, n-pentane, diethyl ether, iso-amyl alcohol -to 1200MPa), Owen and Brinkley^{6,7} (application of Tait and Born equations, Tamman hypothesis, and other considerations), Jacobs and Lawson⁸ (analysis of pressure and density dependence of ϵ), Scaife⁹ (pressure dependence of dielectric properties - eugenol, glycerol, water), Mopsik¹⁰ (n-hexane to 200 MPa), Mopsik¹¹ (carbon tetrachloride, carbon disulfide, isopentane, toluene - to 200 MPa), Hartmann, Neumann, and Rinck^{12,13} (n-hexane, benzene, carbon tetrachloride, chlorobenzene, methanol, benzyl alcohol, acetone, nitrobenzene - to 180 MPa), Hartmann and Schmidt^{14,15} (20 liquids to 75 MPa), Skinner, Cussler, and Fuoss¹⁶ (13 liquids to 500 MPa), Brazier and Freeman¹⁷ (7 hydrocarbons plus carbon tetrachloride), Schornack and C. A. Eckert¹⁸ (chlorobenzene, ethyl acetate, isopropyl ether,

tetrahydrofuran, dichloromethane), and Gee and Freeman¹⁹ (10 organics: perfluoroalkanes, cycloalkanes, benzenes, sulfides). However, only Danforth³, Chang⁵, Mopsik^{10,11}, Skinner, et al.¹⁶, Brazier and Freeman¹⁷, and Schornack and Eckert¹⁸ provide accompanying densities with ϵ for easy evaluations, also remembering that all above studies are for temperatures below 100°C.

For water at temperatures above 100° C, numerous experimental, theoretical, and extrapolative studies of dielectric constant have been presented to pressures of 1000 MPa and temperatures from -35°(metastable liquid) to near 600°C from 1956 starting with those of Franck²⁰ followed by Quist and Marshall,²¹ and through 1997.²²⁻²⁵ All measurements and evaluations for water have been excellently correlated by Fernández, Goodwin, Lemmon, Levelt Sengers, and Williams²³ in their presenting equations and tables for values of ϵ over temperature and pressure ranges from -38° to 927°C and to 1200 MPa. Their extensive correlation is accepted as an International Standard by the International Association for the Properties of Water and Steam^{24,25}. From their correlation, an extended form of Eq. (1) below was developed recently and applied to describe the dielectric susceptibility of water over its entire range of evaluation with a minimum of constants.²⁶ This description for water became even simpler with $(\epsilon - 1)$ approaching at all temperatures (-35 to 927°C) a limiting unit proportionality with density at the approach to zero liquid density.

An excellent study presenting experimentally determined dielectric constants for benzene, water, and their solution mixtures from 25.7° to 400°C and pressures to 300 MPa is that of Deul and Franck.^{27,28} Their study is believed to provide the only excellent determinations and correlations of dielectric constants for an organic liquid that reach up to a 4 times isothermal change in density at supercritical temperatures versus 1.4 times below 100°C. Moreover, the two liquids are greatly dissimilar: highly polar water versus essentially non-polar benzene. This present study evaluates in particular the wide changes in dielectric constants for these two dissimilar liquids by comparing fits from several earlier equations that apply equally well over short ranges of density at low temperatures.

These comparisons show that only Eq. (1) describes satisfactorily at constant temperature these dielectric constants for water and benzene over the wide ranges of density.

II. COMPARING DENSITY EQUATIONS FOR DIELECTRIC CONSTANT

The equation presented here describes the dielectric constant (ϵ) expressed as dielectric susceptibility ($\epsilon - 1$) to be isothermally proportional to the density(ρ) raised to a constant power, given in logarithmic form,

$$\log (\epsilon - 1) = A + B \log \rho \quad (1)$$

Several equations presented previously to express ϵ as a function of density are:

Jacobs and Lawson (1952)⁸:

$$\log \epsilon = A + B \log \rho \quad (2)$$

Skinner, Cussler, and Fuoss(1968)¹⁶:

$$\epsilon = A + B \rho \quad (3)$$

Mopsik(1969)^{10,11}, applying Clausius-Mossotti relation (CM):

$$CM = A + B\rho \quad (4)$$

Owen (1944)⁷:

$$1/\epsilon = A + B (1/\rho) \quad (5)$$

where A and B are constants having different values for each equation when each is fitted to the same experimental data by applying least squares²⁹.

Plots of $\Delta \epsilon$ (Calc. – Obs.) given in Figures 1-4 show comparative fits for each equation for experimental data for water at 25 and 387 and extrapolated at 927°C, and benzene at 400°C^{27,28} over wide ranges of isothermal densities and dielectric constants, with only Eq. (1) providing an acceptable fit over the entire ranges. The values for pure water at 25 and 387 and extrapolated at 927°C were obtained from the formulation and tables of Fernández, et al.,²³⁻²⁵ also represented elsewhere by another equation essentially within the uncertainties of the Fernández, et al., values.²⁶ Those values of ϵ for pure benzene at 400°C were at pressures from 0.1 to 300 MPa.²⁷

Values of ϵ for H₂O at 25 °C below a density of 1 g cm⁻³ were extracted from those of dioxane-water solutions at pressures from 0.1 to 400 MPa as described in detail.²⁶ There are greater uncertainties in the derived experimental values in dioxane-water solutions, and this accounts for the greater random scatter in $\Delta \epsilon$. The representative values at 387 and 927 °C were described for pressures up to 1200 MPa necessary to provide the wide range of densities.

Experimental data evaluated by Fernández, et al., (IAPWS Standard)²³⁻²⁵ in deriving their formulation were available only to 600°C, and they specifically qualified the accuracy of their formulation for values above 600°C given in their Tables 19 and 20.²³ Thus, the agreement in fitting Eq. (1) at 927°C (Fig. 3) seems very good, but with a small divergence at the highest density ($\Delta \epsilon = 0.2$) perhaps from increasing extrapolative uncertainty in ϵ at 927°C at the highest densities. At these extremes, the form of Eq. (1) might be more accurate than the IAPWS formulation^{23, 24} given the successful straight-line fitting throughout by Eq. (1) as shown in Figs. 1-4 and presented later in Figs. 5-8.

III. THE DIFFERING FITS TO DATA IN FIGURES 1-4

One may wonder why so many different forms of equations were proposed for fitting values of ϵ , as presented in the past. Over these times (1930-1956) the only values of ϵ available for liquids were those below 100 °C, where for the liquids studied their densities could be changed by high pressures at most about 10 % in the ranges of 0.8 to 1.0 g/cm³ for

the liquids. With maximum changes in density of 10 %, and generally with values of ϵ above 50 for the polar liquids studied, any one of Eqs. (1-5) could easily fit data within small uncertainties. Consequently, investigators introduced differently derived equations in obtaining essentially the same fits as previous, and distinguishing between fits was essentially impossible.

With the Frank (1956)²⁰ and Quist-Marshall (1965)²¹ equations, based on favored existing theory, estimates of ϵ for water were the first made to high temperatures and pressures into the supercritical region where density could approach zero. Many experimental studies of ϵ for water to these extreme conditions later were published, as extensively correlated by the equation of Fernández, et al.^{23,24}

These studies have now provided values of ϵ for water over wide ranges that were applied here in testing the several previously published theoretical equations in comparing fits as shown in Figs. 1-4. Values of ϵ at 25°C are those of Marshall²⁶ to low densities in dioxane-water solutions and from the Fernández, et al.,^{23, 24} equation to high pressures. Deul and Franck^{27,28} provided highly accurate values of ϵ for benzene at temperatures to 400 °C and at pressures to 300 MPa.

Thus there are now data for dielectric constant of liquids that span wide ranges of temperature and density. With these data one can re-evaluate the previous several earlier proposed equations for description of ϵ and compare their fits with Eq. (1) proposed here that provides rationality by applying dielectric susceptibility ($\epsilon - 1$) instead of ϵ in describing changes in ϵ with density. Use of dielectric susceptibility allows its approach to zero as density approaches zero rather than unity for ϵ at this limit.

In evaluating the fits in Figs 1-4, the ranges of ($\epsilon - 1$) must be considered. For example, where values of ($\epsilon - 1$) are generally in the high range, there is little difference in fit in applying Eq. (1) or (2), where the only difference is applying ($\epsilon - 1$) instead of ϵ , and this closeness in fit is observed in Fig. 1. There are marked differences in fit for Eqs. (1) and (2) where ϵ lies in the ranges 3-28, 2-16, and 1.65-2.2, respectively, as shown in Figs. 2-4.

IV. THE OWEN-BRINKLEY EQUATION RELATING ϵ TO PRESSURE

Owen and Brinkley proposed applying the Tait equation that would allow calculation of ϵ from pressure(P),^{6,7} and their equation is given,

$$1 / (\epsilon - 1) = A + B \log [(C + P) / (C + 1)] \quad (6)$$

where A and B , and C are constants and P is pressure. As Eqs. (2-5) deviate over wide ranges of densities, the Owen-Brinkley equation also deviates greatly over these ranges as shown in Fig. 5 for water, but with a very close fit by Eq. (1) over all densities. The constants for fitting Eqs. (1) and (6) were obtained over a very short range of $(\epsilon - 1)$ from 18 to 22, and were applied widely outside that range as shown in Fig. 5 in emphasizing the extrapolative validity of Eq. (1).

V. Log ($\epsilon - 1$) FOR HEXANE AND BENZENE DESCRIBED BY COMMON STRAIGHT-LINE FROM -50 TO 400 °C, 0.5 TO 1 g/cm³

By applying Eq. (1) to data for ϵ of Mopsik¹⁰ for hexane and of Deul and Franck^{27,28} for benzene, Fig. 6 shows all values falling on a common straight line. Adherence of the data to Eq. (1) is further emphasized by the insignificant deviations of either liquid over the entire range of temperature and density as shown in Fig. 7. It is obvious that the previously published relationships could not realistically describe dielectric-constant behavior of these two liquids.

VI. DESCRIPTION OF LIQUIDS BY EQUATION 1, WITH CONSTANTS RELATED TO POLARITY.

Figure 8 shows some representative published dielectric constants for many different liquids over wide ranges of temperature, density, and pressure plotted according

to the Marshall Eq. (1). One notes the commonality of different liquids according to similar molecular polarities, and these are reflected in the intercept and slope constants of Eq. (1). Intercept A is highest for high polarity liquids (water) while slope B is closely the same for similar-class liquids while even being roughly the same for all the liquids shown. Also for water, an increasing temperature (kinetic energy) decreases its strong intermolecular interactions (increasing randomness) that decreases polarization capacity indicated by a decreasing ϵ at constant density. The constants A and B together with standard deviations of fit determined by least squares²⁹ are given in Table 1.

All hydrocarbons fall essentially on a common straight-line (except toluene), with benzene and hexane on the same line to 400 °C (Figs. 6 and 7). This essentially single slope and intercept for these hydrocarbons should extend over wide ranges of temperature as already confirmed for benzene and hexane. Toluene with its slightly higher polar methyl group has a slightly increased intercept from the other hydrocarbons but with essentially the same slope.

The ethers fall together, with the greater polarized alcohols, acetate, and dichloromethane falling separately. Finally, symmetrical carbon disulfide and carbon tetrachloride, with very low polarities, fall nearly in line with the hydrocarbons but at higher densities. These high quality dielectric constants all adhere well to Eq. (1) and fall at rationally reasoned positions with relation to expected degrees of liquid polarity.

VII CONCLUSION

Equation (1) is shown here to describe accurately isothermal dielectric susceptibilities of fluids over the widest presently accessible ranges of experiment. In contrast, past theoretical equations for this property are very limited in their range and should be rejected in favor of Eq. (1). The two-constant Eq. (1) shows that fluids with low dielectric susceptibility such as hydrocarbons are temperature independent throughout experiment, generally from -50° to $+30^{\circ}$ C, and based on benzene behavior would be expected to show this independence to very high temperatures. The separate organics,

benzene and hexane, are even described by a common line from -50 to $+400^{\circ}\text{C}$ as a function only of density over the entire range of experiments. It seems that any proposed new theory for dielectric constant behavior must now accept the framework of Eq. (1) (applying Occam's razor) in theoretically predicting values of A and B with respect to fluid molecular dipole moments, density, and temperature. With future experiments, it may be shown that all liquids (fluids) at very low decreasing densities approach an even simpler limiting unit proportionality to density, as observed for water.²⁶ This study seems to satisfy the recent concluding comments by Ball³⁰ on searching for a broad understanding of water in trying to resolve some of its mysteries, and also the proposals of Weingartner and Franck in this same direction.³¹

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Table 1. Property ranges for liquid behaviors shown in Fig. 7 and deviations from the Marshall Eq. (1).

Ref.(Fig.8)	Liquid (ϵ)	Ranges			Constants		Std. Dev.
		$T/^\circ\text{C}$	P/MPa	$\rho/(\text{g}/\text{cm}^3)$	A	B	$\Delta \log (\epsilon - 1)$
C ²⁶	water and in dioxane (14-104)	25	0.1-1000	0.25-1.23	1.889	1.231	0.65
D ²³	water (3.83-28.49)	387	0.1-1200	0.25-1.00	1.438	1.569	0.069
E ²³	water (2.48-15.34)	927	0.1-1200	0.25-1.00	1.161	1.633	0.092
F ¹⁰	n-hexane (1.88-2.10)	-50 to 25	0.1-200	0.65-0.78	0.1732	1.244	0.001
G ¹⁷	n-pentane (1.83-2.13)	30	0.1-400	0.62-0.79	0.1789	1.229	0.003
H ¹¹	isopentane (1.83-2.07)	-50 to 25	0.1-200	0.61-0.76	0.1805	1.245	0.001
I ¹⁷	cyclopentane (1.96-2.24)	30	0.1-400	0.74-90	0.1478	1.235	0.002
J ¹⁷	2-2 dimethylbutane (1.86-2.14)	30	0.1-400	0.64-0.80	0.1801	1.264	0.005
K ¹⁷	methylcyclohexane (2.01-2.24)	30	0.1-400	0.76-0.91	0.1429	1.161	0.002
L ¹⁷	n-octane (1.93-2.15)	30	0.1-400	0.69-0.84	0.1474	1.111	0.002
M ₁ ^{27,28}	benzene (2.27-2.36)	25.7	0.1-400	0.87-92	0.1781	1.244	0.001
M ₂ ^{27,28}	benzene (1.67-2.20)	400	0.1-400	0.52-84	0.1676	1.210	0.001
N ¹¹	toluene (2.38-2.71)	-50 to 25	0.1-200	0.86-1.00	0.2316	1.419	0.020
O ³	diethyl ether (4.15-7.68)	30	0.1-1200	0.72-1.05	0.7849	2.033	0.029
P ¹⁸	isopropyl ether (3.81-5.77)	30	0.1-500	0.71-0.92	0.7461	2.024	0.014
Q ¹⁸	tetrahydrofuran (7.26-9.46)	30	0.1-500	0.87-1.06	0.8850	1.501	0.002
R ³	ethanol (23.2-33.7)	30	0.1-1200	0.78-1.07	1.475	1.216	0.156
S ¹⁸	ethyl acetate (5.98-7.60)	30	0.1-500	0.89-1.10	0.7631	1.262	0.001
T ¹⁸	dichloromethane (8.65-10.71)	30	0.1-500	1.31-1.55	0.7201	1.401	0.015
U ¹¹	carbon disulfide (2.63-3.06)	-50 to 25	0.1-200	1.25-1.48	0.0714	1.428	0.002
V ¹¹	carbon tetrachloride(2.18-2.40)	0, 50	0.1-200	1.54-1.75	-0.1716	1.304	0.001

LIST OF FIGURES

Fig. 1. $\Delta\epsilon$ (Calcd. – Obs.) vs ϵ (dielectric constant, water) at 25°C in dioxane solutions and for pure water at $\epsilon = 78.47$ and above. Applying different equations for ϵ .

Fig. 2. $\Delta\epsilon$ (Calcd. – Obs.) vs ϵ (dielectric constant, water) at 387°C applying different equations.

Fig. 3. $\Delta\epsilon$ (Calcd. – "Obs.") vs ϵ (dielectric constant, water) at 927°C, qualified by Fernández, et al., (Ref. 23, Table 19) since 327°C above experiments. Applying different equations. Marshall Eq. (1) agreement seems good (see text).

Fig. 4. $\Delta\epsilon$ (Calcd – Obs) vs ϵ (dielectric constant, benzene) at 400°C. Applying different equations.

Fig. 5. Test of Owen-Brinkley equation; water at 402°C. Comparison of dielectric constant (ϵ) fit with Marshall Eq. 1.

Fig. 6. $\text{Log}(\epsilon - 1)$ vs log density for hexane and benzene, -50 to +400°C

Fig. 7. $\Delta\epsilon$ (Calcd – Obs) vs density for benzene and hexane, -50 to +400°C.

Fig. 8. $\text{Log}(\epsilon - 1)$ vs log density for water and many organic liquids, -50 to +927°C.

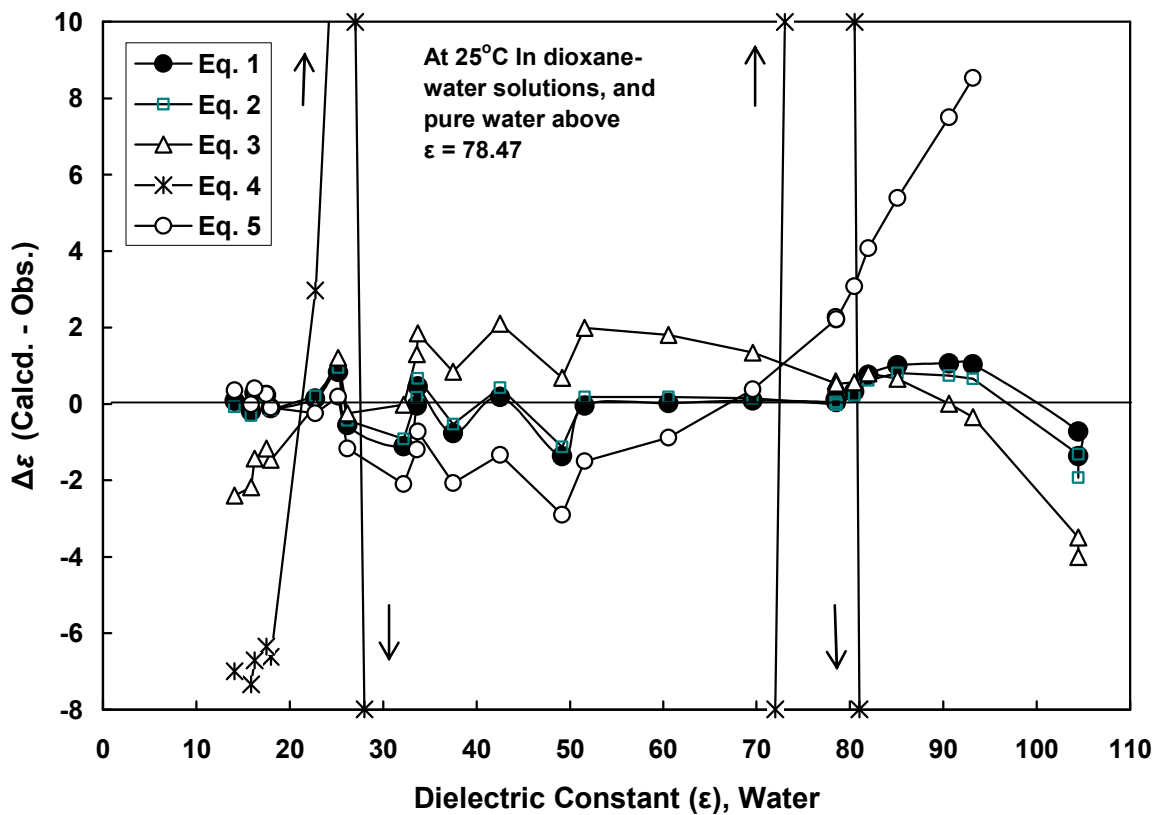


Fig. 1. $\Delta\epsilon$ (Calcd. - Obs.) vs. ϵ (dielectric constant, water) at 25°C in dioxane-water solutions and for pure water at $\epsilon = 78.47$ and above. Applying different equations for ϵ .

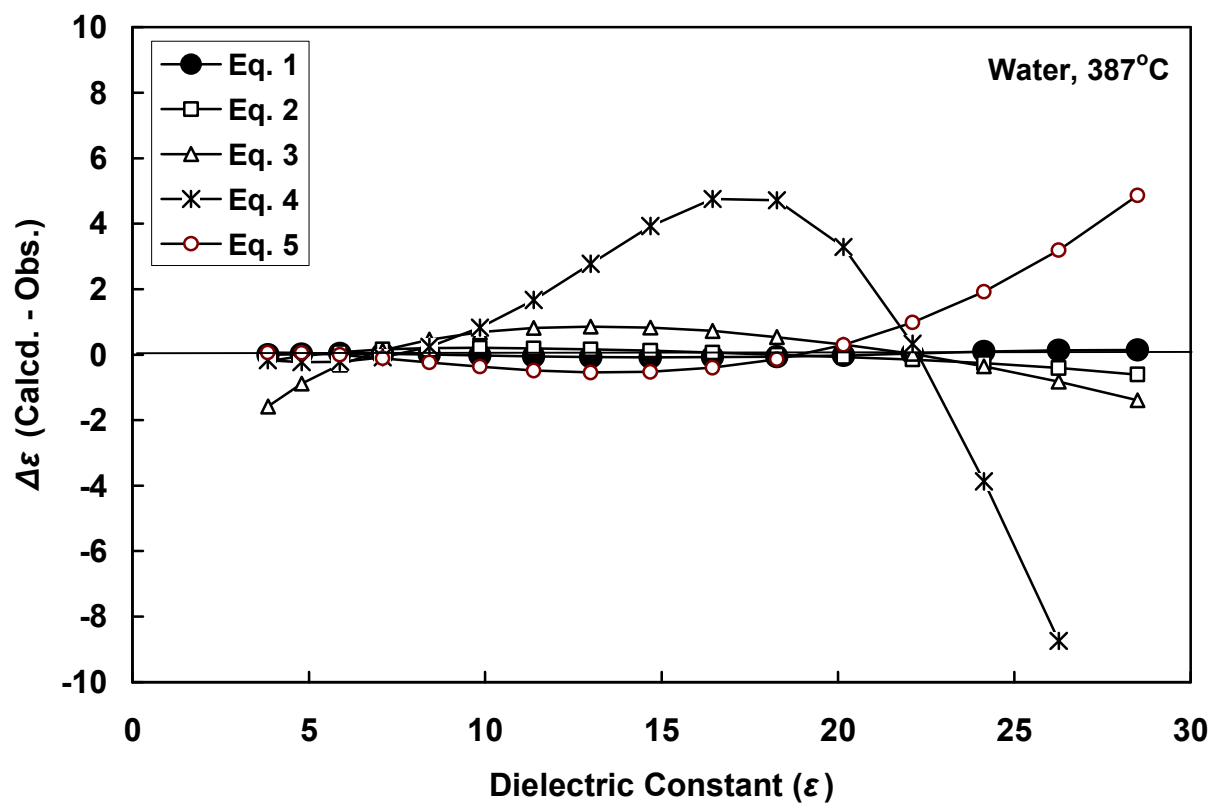


Fig. 2. $\Delta\epsilon$ (Calcd. - Obs.) vs ϵ (dielectric constant, water) at 387°C applying different equations.

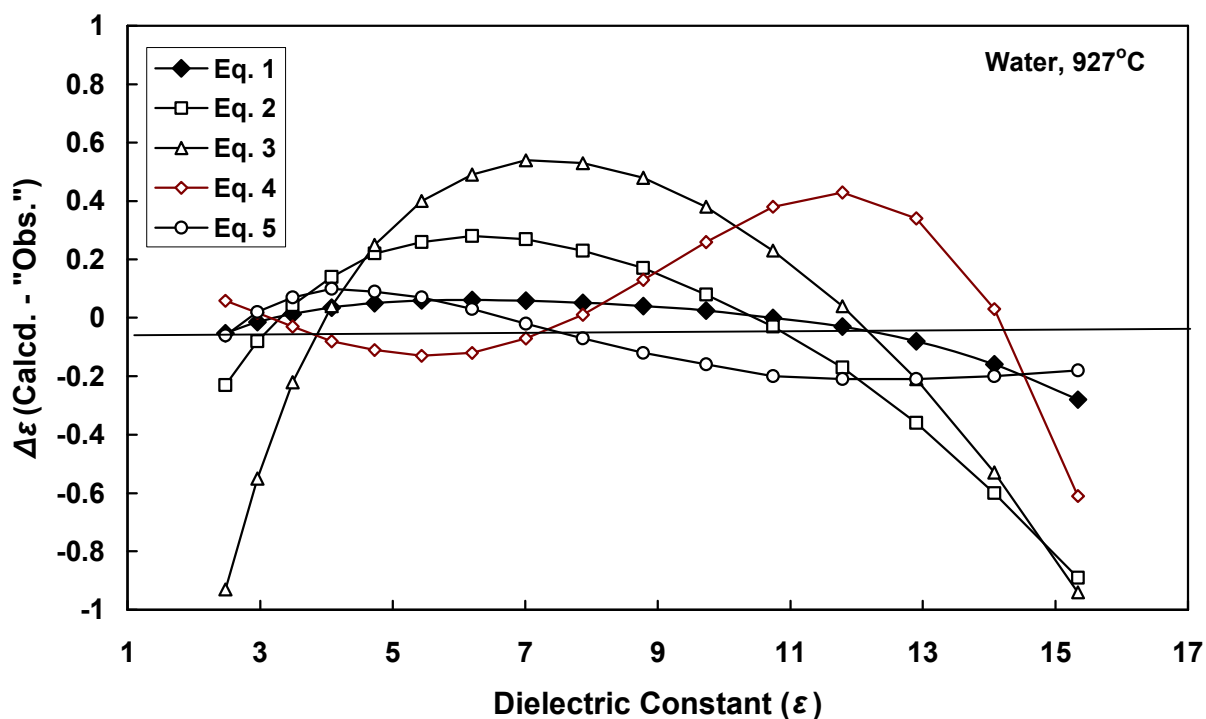


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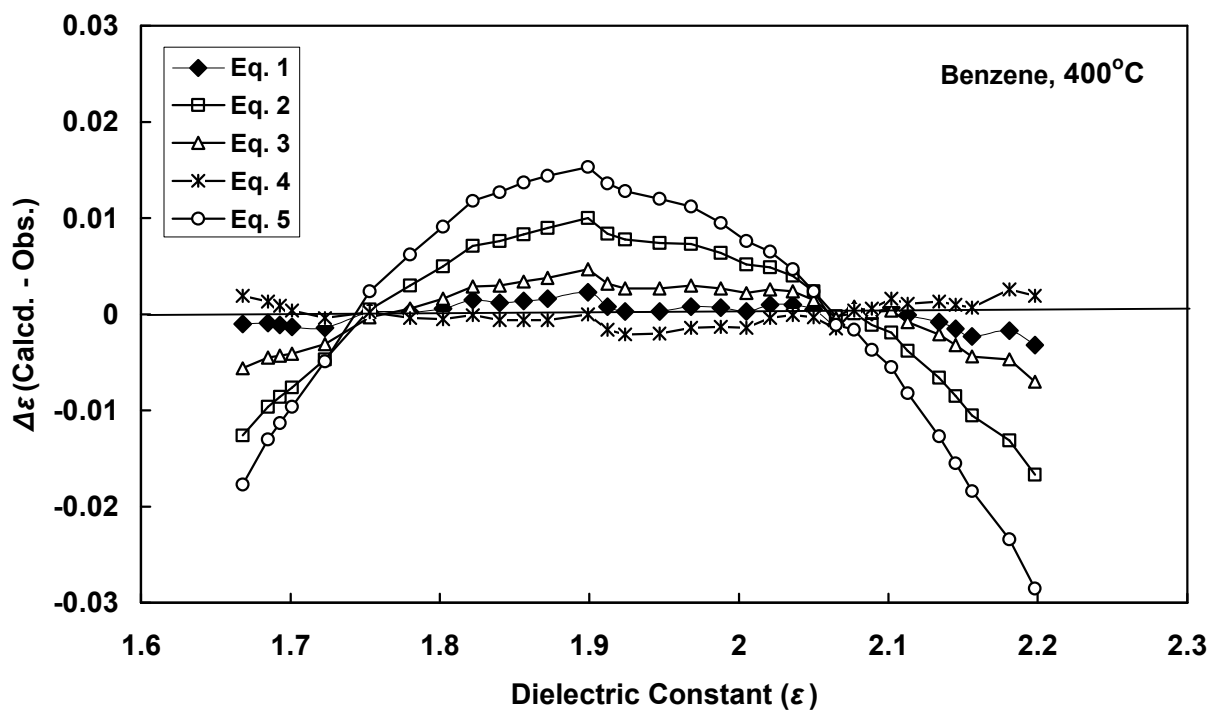


Fig. 4. $\Delta\epsilon$ (Calcd. - Obs.) vs ϵ (Benzene) at 400°C. Applying different equations.

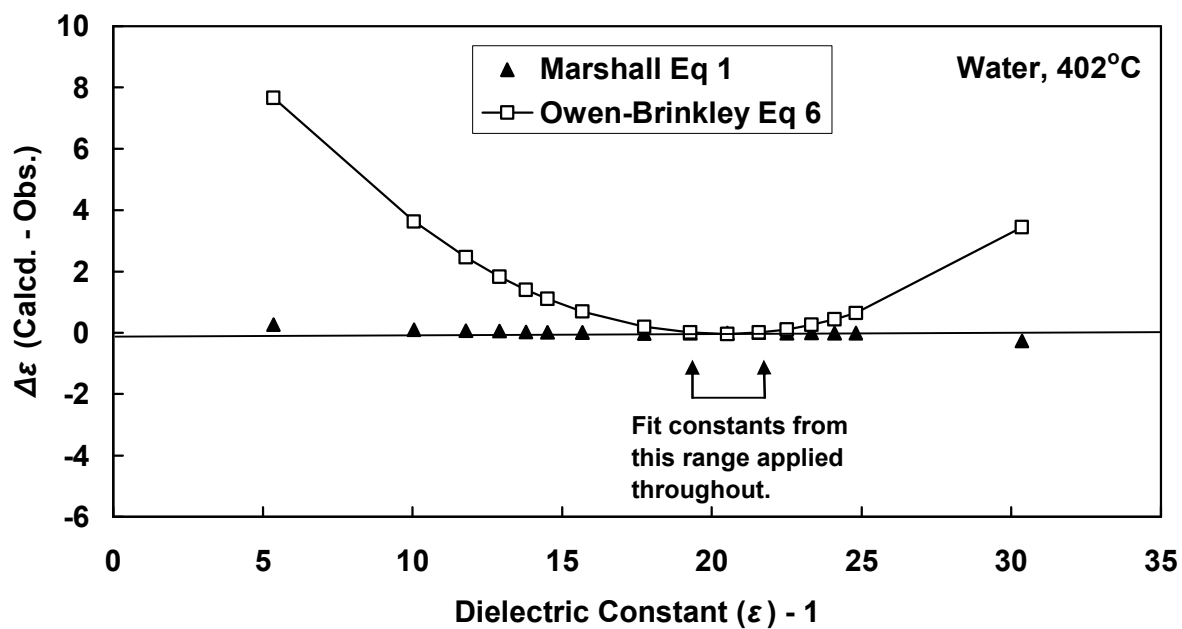


Fig. 5. Test of Owen-Brinkley equation - water- 402°C. Comparison with Marshall Eq. 1.

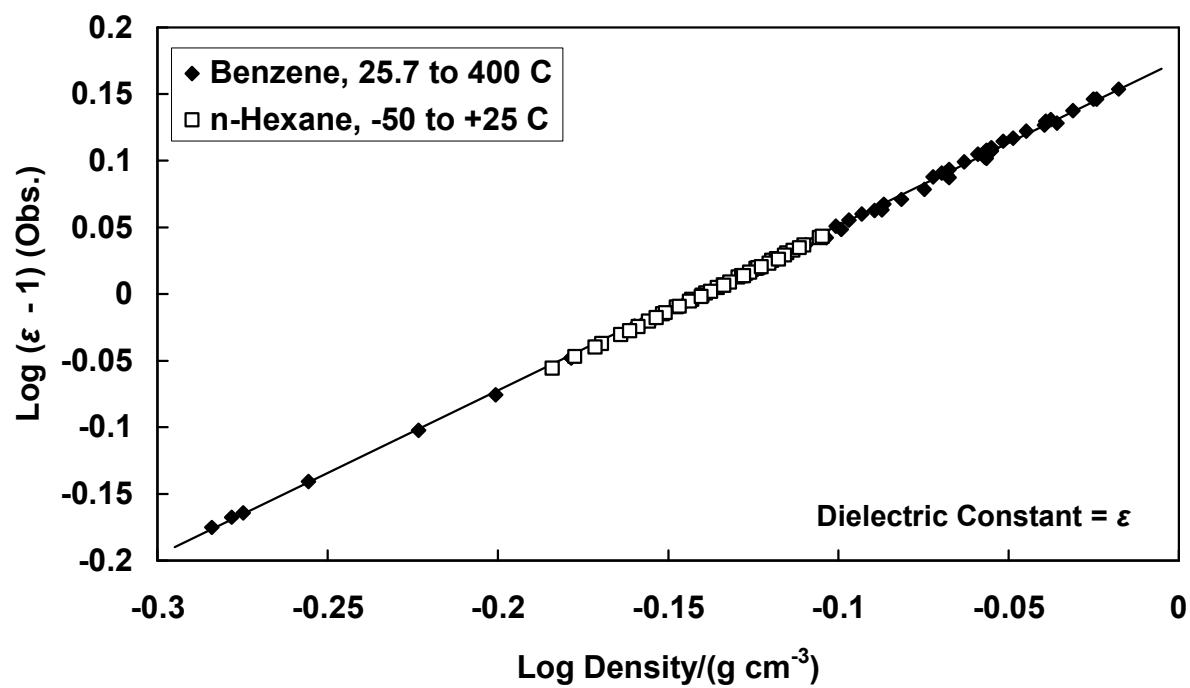


Fig. 6. Log ($\epsilon - 1$) vs log density/(g cm⁻³) for benzene and n-hexane, -50 to 400°C.

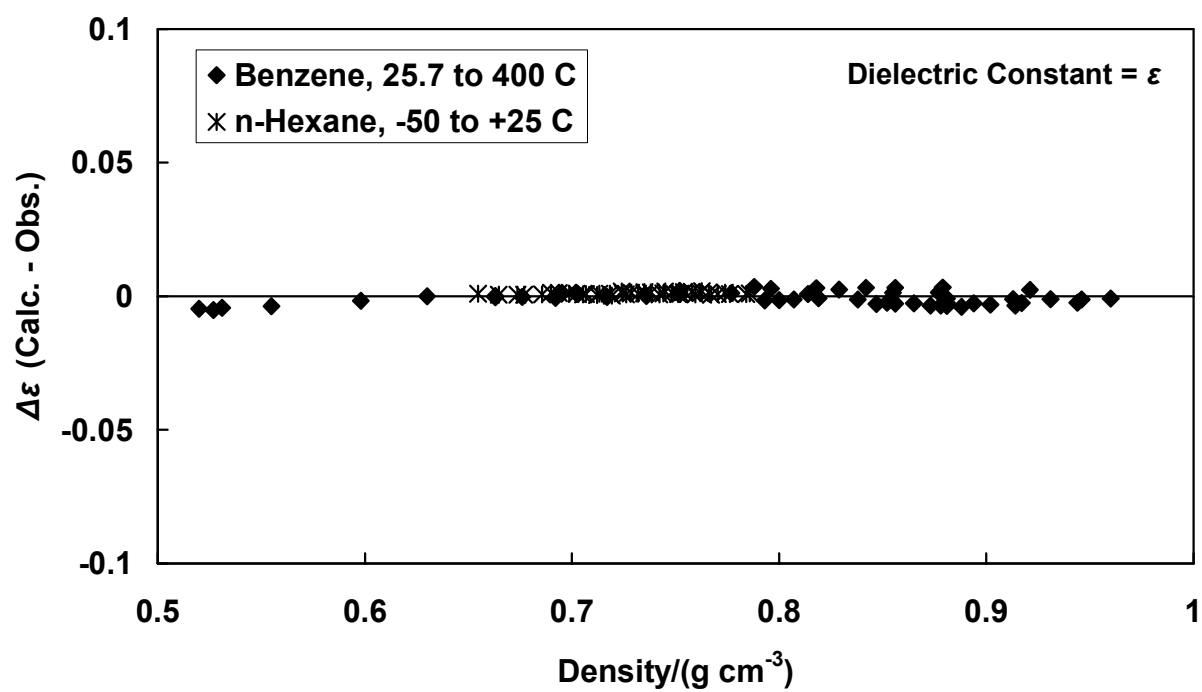


Fig. 7. $\Delta\epsilon$ (Calcd. - Obs.) vs. density for benzene and n-hexane, -50 to 400°C.

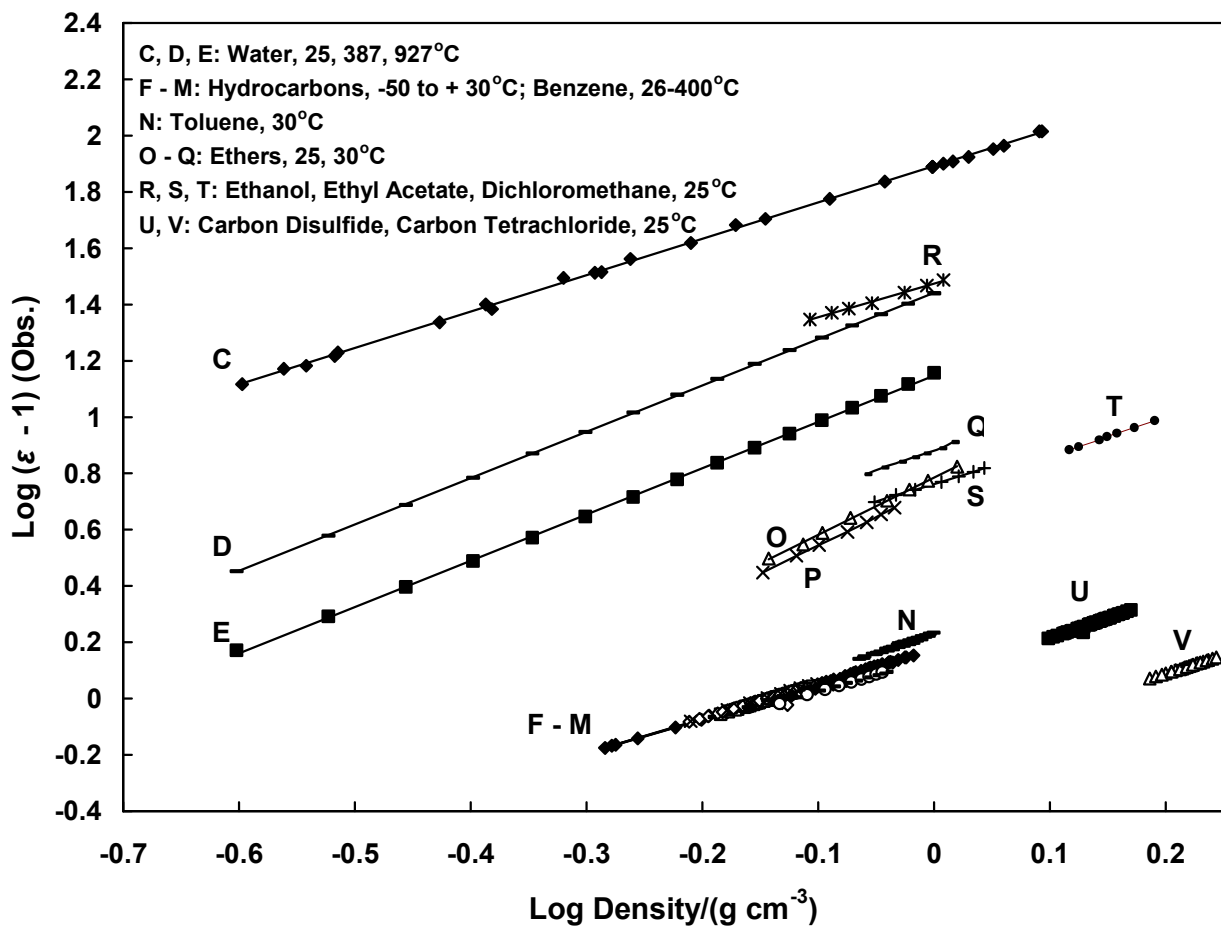


Fig. 8. $\text{Log}(\epsilon - 1)$ vs $\text{log density}/(\text{g cm}^{-3})$ for water and many organic liquids, -50 to 927°C.