

# Dielectric Constant and Polarization

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## Background information and definitions

The electric dipole moment ( $\mu$ ) of a molecule is directed from the center of negative charge ( $-q$ ) to the center of positive charge ( $+q$ ) distance  $r$  away. The units are usually given in Debye ( $= 3.336 \times 10^{-30} \text{ C m}$ ).

$$\mu = qr$$

In liquid water, molecules possess a distribution of dipole moments (range  $\sim 1.9 - 3.1 \text{ D}$ ) due to the variety of hydrogen bonded environments.

If two charges  $q_1$  and  $q_2$  are separated by distance  $r$ , the (Coulomb) potential energy is  $V$  (joule)

$$V = \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

where  $\epsilon_0$  is the [permittivity of a vacuum](#) ( $= 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$ ; the ability of a material to store electrostatic energy).

In a medium it is lower

where  $\epsilon$  is the medium's permittivity.

$$V = \frac{q_1 q_2}{4\pi\epsilon r}$$

The dielectric constant ( $\epsilon_r$ ) of the medium (also known as the relative permittivity) is defined as

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}$$

and clearly approaches unity in the dilute gas state. In liquid water, it is proportional to the mean-square fluctuation in the total dipole moment. In liquid water, the [dielectric constant is high](#) and there is a linear correlation between it and the number of [hydrogen bonds](#) [239].

## Polarization and polarizability

The polarization ( $P$ ) of a substance is its electric dipole moment density ([see also](#)). The charge density vector ( $D$ ) is the sum of the effect of the applied field and the polarization.

$$D = \epsilon_0 E + P$$

But as

([see variation with applied field](#))

$$D = \epsilon E$$
$$P = (\epsilon_r - 1)\epsilon_0 E$$

The dielectric constant ( $\epsilon_r$ ) is related to the molar polarization of the medium ( $P_m$ ) using the Debye equation

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho P_m}{M}$$

where  $\rho$  is the mass density ( $\text{kg m}^{-3}$ ),  $M$  is the molar mass (kg). At high dielectric constant, such as water, the left hand side of the above equation approximates to unity and the molar polarization (calculated from equation(1) below =  $181.5 \times 10^{-6} \text{m}^3$  at 25 °C) should approximate to the molar volume ( $18.0685 \times 10^{-6} \text{m}^3$  at 25 °C) but it clearly does not in the case of water. The molar polarization of the medium ( $P_m$ ) is defined as

$$P_m = \frac{N_A}{3\epsilon_0} \left( \alpha + \frac{\mu^2}{3kT} \right) \quad (1)$$

where  $\alpha$  is the polarizability of the molecules, which is the proportionality constant between the induced dipole moment  $\mu^*$  and the field strength  $E$  ( $\mu^* = \alpha E$ ),  $N_A$  is the [Avogadro number](#),  $k$  is the [Boltzmann constant](#) ( $=R/N_A$ ),  $T$  is the absolute temperature and  $\mu$  is permanent dipole moment. Unfortunately, in line with many other [anomalies of water](#), this equation is not a good predictor for the behavior of water, which shows a minimum molar polarization at about 15 °C. The term in ( $\epsilon_r + 2$ ) comes from the relationship between the local field ( $E'$ ) and the applied field ( $E$ ).

$$E' = (E/3)(\epsilon_r + 2)$$

The polarizability ( $\alpha$ ) may be given as the polarizability volume ( $\alpha'$ ) where

$$\alpha' = \frac{\alpha}{4\pi\epsilon_0}$$

The second term in [equation \(1\)](#) is due to the contribution from the permanent dipole moment, which is negligible when the medium is non-polar or when the frequency of the applied field is sufficiently high that the molecules do not have time to change orientation. In this case the Clausius-Mossotti equation holds (but again not for water):

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho N_A \alpha}{3M\epsilon_0}$$

**Refractive index**

The refractive index ( $n_r$ ) in the visible and ultraviolet is the ratio of the [speed of light](#) in a vacuum ( $c$ ) to that in the medium ( $c'$ );  $n_r = c/c'$ . It is also related to the relative permittivity ( $\epsilon_r$ ), the absorption coefficient ( $\alpha$ ) and wavelength ( $\lambda$ ) [\[177\]](#).

$$n_r^2 = \epsilon_r + \left( \frac{\lambda \alpha}{4\pi} \right)^2$$

This reduces to  $\epsilon_\infty = n_r^2$  where  $\epsilon_\infty$  is the relative permittivity at visible frequencies ( $4 \times 10^{14}$  -  $8 \times 10^{14}$  Hz,  $n_r \sim 1.34$ ) and  $\epsilon_s = n_r^2$  where  $\epsilon_s$  is the relative permittivity at low frequencies (static region;  $< 10^9$  Hz,  $n_r \sim 9$ ). It also follows that, as the temperature is raised,  $\epsilon_r$  tends towards  $n_r^2$  [\[423\]](#).

Source: <http://www1.lsbu.ac.uk/water/microwav2.html>