

Dielectric Constant and Polarization

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Background information and definitions

The electric dipole moment (μ) 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 ϵ_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 ϵ is the medium's permittivity.

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

The dielectric constant (ϵ_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 (ϵ_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 ρ is the mass density (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 α is the polarizability of the molecules, which is the proportionality constant between the induced dipole moment μ^* 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 μ 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 (α) may be given as the polarizability volume (α') 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 (ϵ_r), the absorption coefficient (α) and wavelength (λ) [177].

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

This reduces to $\epsilon_\infty = n_r^2$ where ϵ_∞ is the relative permittivity at visible frequencies (4×10^{14} - 8×10^{14} Hz, $n_r \sim 1.34$) and $\epsilon_s = n_r^2$ where ϵ_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, ϵ_r tends towards n_r^2 [423].

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