Dielectric Constant and Polarization

**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 ($= 3.336 \times 10^{-30}$ C m).

$$\mu = qr$$

In liquid water, molecules possess a distribution of dipole moments (range ~1.9 - 3.1 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)

$$V = \frac{q_1 q_2}{4\pi \varepsilon_0 r}$$

where $\varepsilon_0$ is the permittivity of a vacuum ($= 8.854 \times 10^{-12}$ C$^2$ J$^{-1}$ m$^{-1}$; the ability of a material to store electrostatic energy).

In a medium it is lower

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

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

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

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$

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.

$$D = \varepsilon_0 E + P$$
But as

\[ D = \varepsilon E \]
\[ P = (\varepsilon_r - 1)\varepsilon_0 E \]

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

\[ \frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho P_m}{3M} \]

where \( \rho \) 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) at 25 °C should approximate to the molar volume (18.0685x10\(^{-6}\) 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

\[ P_m = \frac{N_A}{3\varepsilon_0} \left( \alpha + \frac{\mu^2}{3kT} \right) \]

(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, \( M_k \) 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 (\( \varepsilon_r + 2 \)) comes from the relationship between the local field (\( E' \)) and the applied field (\( E \)).

\[ E' = (E/3)(\varepsilon_r + 2) \]

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

\[ \alpha' = \frac{\alpha}{4\pi\varepsilon_0} \]

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):

\[ \frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho N_A \alpha}{3M\varepsilon_0} \]

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

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

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

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