

The Debye and inverse Debye equations

The Debye equation is as follows:

$$\varepsilon = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + j\frac{f}{f_D}} \quad (1)$$

where

f is the frequency

ε_s is the static permittivity ($f \rightarrow 0$);

f_D is the Debye relaxation frequency[†].

ε is the complex (relative) permittivity $\varepsilon' - j\varepsilon''$;

ε_{∞} is the (fictitious) permittivity for $f \rightarrow \infty$; and

The inverse Debye equations become

$$f_D = \frac{f \cdot (\varepsilon' - \varepsilon_{\infty})}{\varepsilon''} \quad \varepsilon_s = \varepsilon' + \varepsilon'' \cdot (f/f_D) \quad (2)$$

The Cole-Cole and inverse Cole-Cole equations

The equation becomes

$$\varepsilon = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + \left(j\frac{f}{f_D}\right)^{1-\alpha}}, \text{ where } \alpha \text{ is the so-called distribution parameter.} \quad (3)$$

The exponent $(1-\alpha)$ of the imaginary term $[j \cdot (f/f_D)]$ has firstly to be interpreted. The general equation for this type of expression is

$$z^{\delta} = |z|^{\delta} \cdot [\cos(\delta\theta) + j\sin(\delta\theta)], \text{ where } \theta = \arctan(\text{Im}z/\text{Re}z) \quad (4)$$

Hence, the result becomes an amplitude change and a rotation in the complex plane. Since we know that α is small and we also want to algebraically separate real and imaginary terms, the following is obtained:

$$\left(j\frac{f}{f_D}\right)^{1-\alpha} = jA(1-j\gamma), \text{ where } \beta = 90 \cdot (1-\alpha)^\circ; \quad A = \left(\frac{f}{f_D}\right)^{1-\alpha} \cdot \sin\beta \quad \text{and} \quad \gamma = \cot\beta \quad (5)$$

Separation of real and imaginary terms and insertion then gives, in analogy with the inverse Debye equations

$$A = \frac{\varepsilon''}{\varepsilon' - \varepsilon_{\infty} - \varepsilon''\gamma} \quad \text{and} \quad \varepsilon_s = \varepsilon' + A[\varepsilon'' + \gamma(\varepsilon' - \varepsilon_{\infty})] \quad (6)$$

The second equation (6) directly gives the desired ε_s . Insertion of the calculated A from the first eq. (6) back into the second equation (5) and inverting it then gives the desired f_D .

It is to be noted that there are two “unknowns” in the Cole-Cole representation: ε_{∞} and α . These have to be obtained by comparisons of resulting ε_s and f_D by trial-and-error calculations using measurements at several frequencies and the same temperature.

[†] It is also common to characterise the property by a “critical” wavelength $\lambda_c (= c/f_D)$, where c is the speed of light, or by a “characteristic relaxation time” $\tau (= 1/(2\pi f_D))$. f_D is chosen here, since it the easiest to use in qualitative considerations.

The choice of reference liquids

Desirable properties of a reference liquid are: representativity for expected practical load substances; reasonably non-hazardous; stable; a low vapour pressure at room temperature; reasonably inexpensive and common; to be obtainable with high purity and the impurities not influencing the permittivity much.

Water is of course a primary choice; it possesses all these properties and is the liquid having by far the best available literature data on microwave permittivity. It can therefore be used for certain calibrations of dielectric measurement equipment which is subsequently used with other liquids. **OWN DATA EXIST**

Other reference liquids should not absorb ambient water vapour. As an example, the moisture absorption criterion excludes pure methanol and ethanol. In spite of this, there are reports of these liquids being used for calibrations of equipment of the open coaxial probe type.

The criteria should also include a spread in permittivity between the chosen liquids. Water has an ϵ' of almost 80 in the ISM frequency range of major interest (about 900...2500 MHz). The choices of ϵ' must consider that the effective wavelength contraction is proportional to $\sqrt{\epsilon'}$ and the power penetration depth d_p is roughly proportional to $\sqrt{\epsilon'/\epsilon''}$, but also the practical need for a substance with data close to those which are to be routinely measured or used. When all criteria above are applied, the choice becomes limited to only a handful pure liquid compounds. *A list on which the choices below was based is given on the next page.*

1-octanol ($\text{CH}_3(\text{CH}_2)_7\text{OH}$) is a proper choice as low- ϵ' reference liquid. Rather good but old literature data are available. It is obtainable with >99,5 % purity and <0,1 % H_2O , and the major residual constituent is 2-octanol ($\text{CH}_3(\text{CH}_2)_5\text{CH-OH-CH}_3$) which has quite similar dielectric properties. Approximate literature data at +20 °C are $\epsilon = 3,17 - j0,71$ at 900 MHz and $\epsilon = 3,10 - j0,26$ at 2450 MHz.

Pyridine ($\text{C}_5\text{H}_5\text{N}$) is a proper choice as medium- ϵ' reference liquid. Old literature data are available. It is obtainable with >99,5 % purity and <0,1 % H_2O , with the major residual constituent being α -picoline (H in the benzene ring position nearest to the N being replaced by CH_3), which has rather similar ϵ_s (static, $f=0$) to pyridine. Own reference data at +20 °C are $\epsilon = 13,39 - j0,34$ at 900 MHz and $\epsilon = 13,32 - j0,92$ at 2450 MHz. **OWN DATA EXIST**

DMF (dimethylformamide) ($\text{HCON}(\text{CH}_3)_2$) is a proper choice for a high- ϵ' and low- ϵ'' reference liquid. Some scattered literature data exist, as well as unpublished data. Own reference data at +20 °C are $\epsilon = 38,09 - j2,01$ at 900 MHz and $\epsilon = 37,35 - j5,36$ at 2450 MHz. The liquid is extensively used in pharmaceutical microwave chemistry and is probably the overall least toxic choice of the special pharmaceutical MW chemistry compounds obtainable with very high purity. DMF is readily obtainable with >99,9 % purity and <0,02 % H_2O . **OWN DATA EXIST**

Methanol-water mixtures can also be used, primarily for obtaining high ϵ' values under conditions of a high $\tan\delta$ at 2450 MHz – similar to the dielectric properties of typical compact food substances. Literature data are available (e.g. $\epsilon \approx 46 - j20$ at 2450 MHz, for 60 % MeOH and 40 % H_2O by volume), but are expected not to be very accurate. Even if these high losses may be favourable for some comparisons, the high dispersion may be a problem but results in a more stable ϵ'' value under temperature variation, at 2450 MHz. The mixing inaccuracy is an additional source of error, but should be small. The risk of stronger evaporation of methanol than water during handling must, however, be observed. Own reference data of a mixture with 54 % MeOH by weight (and 46 % H_2O), $\epsilon = 51,87 - j9,22$ at 915 MHz and $43,10 - j20,08$ at 2450 MHz. **OWN DATA EXIST FOR 54% MeOH BY WEIGHT**

Substance	ϵ at 20...25 °C and 2450 MHz	ϵ at 40...50 °C and 2450 MHz	ϵ at 20...25 °C and 900 MHz	Water content of comm. available product (%)	Vapour pressure @ 20°C (kPa)	Boiling temp (std press.) (°C)	Hazards & other comments
Water	78,1-j10,1	71,1-j5,32	79,3-j3,77	—	2,33	100	Most well known/specified, but has too high ϵ
MeOH	21,5-j13,5	24,1-10,3	30,6-7,8	<1	13,0	65	Too high ϵ'' @ 2450. Absorbs water vapour. Flammable.
46%H_2O+54%MeOH (by weight)	43,5-j19,2	44,8-j10,8	51,5-j8,5		—	—	"Own" mixture. Has minimum ϵ'' change with concentration; ϵ' is approx. prop. to % H_2O , @20°C. 45%MeOH@2,9GHz: $\epsilon=51,3-j20$; 70%: $\epsilon=35,5-j20$
1-propanol	\approx 3,7-j2,5		\approx 6-j3		2,0	97	A harmful contamination of the air will be reached rather slowly on evaporation of this substance at 20°C; on spraying or dispersing, however, much faster.
Isopropanol	\approx 4-j3		7,3-j6,7		4,4	82	Low-risk except with eye contact.
1-butanol	4-j0,87 (?)		(4,65-j4,6)		0,7	118	Low-risk except with eye contact. The standard Buckley-Marryott compilation data give 3,21-j1,89 @ 2450 MHz and 25 °C.
n-butanol	4,11-j1,05				0,56	118	Eye damage risk. Harmful if swallowed.
1-octanol	3,11-j0,29 (2,79-j0,38)	3,16-j0,56	3,2-j0,8		0,013	195	No hazard marks. Eye and skin irritant. May be harmful by ingestion or inhalation. The standard Buckley-Marryott compilation data give 3,11-j0,32 @ 2450 MHz and 25 °C; for 2-octanol: 2,81-j0,28.
1,2-dichloroethane (ethylene dichloride)	10,0-j0,46 @2250MHz	\approx 9,5-j0,4?	\approx 10,2-j1,5	0,01	8,26	83,5	Toxic fumes when burning. See http://www.atsdr.cdc.gov/facts38.html . Smells like gasoline.
Acetone	21,4-j1,02	\approx 20-j0,6	21,5-j0,38		24,6	56	
Dichloromethane (DCM)	9,5-j0,3				47	40	Harmful if swallowed or inhaled. May be harmful by skin contact. Eye and skin irritant. Readily absorbed through the skin. Asphyxiant. Causes CNS depression. Possibly carcinogenic in humans. Remains bound to body fats.
Dimethylformamide DMF	37,1-j5,1	33,9-j3,2	37,8-j1,9		0,347	153	Probably the overall least toxic choice of the MWV chemistry compounds. May have some peculiar permittivity behaviour as function of temperature.
Dimethylsulfoxide (DMSO)	28,4-j6,66				0,053	191	Most hazardous of the MWV chemistry compounds; mutagen. Pungent smell.
Acetonitrile (MeCN)	34,2-2,14				9,73	82	Toxic + flamm.
Ethyl acetate	6,0-j0,27		6,1-j0,14		9,9	77	X + flamm. Acetic acid ethyl ester
Chlorobenzene	\approx 5,6-j0,50		5,62-jx	0,02	1,1	132	X + environm.
1,4-dichlorobenzene	9,76-j1,17				0,17	174	X Measured @ 2250 MHz
Pyridine	13,3-j1,2	12,1-j0,85	13,4-j0,45		2,1	115	X + flamm. C_5H_5N

See safety status at <http://www.itcilo.it/actrav/actrav-english/telearn/osh/kemi/alpha2.htm>