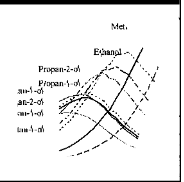
# Dielectric parameters relevant to microwave dielectric heating



CHEMICAL
SOCIETY
REVIEWS

**Camelia Gabriel,[a] Sami Gabriel,[a] Edward H. Grant,[a,b] Ben S. J. Halstead[b] and D. Michael P. Mingos[b]***

[a] *Microwave Consultants Ltd., Woodford, Essex, UK, E18 2EL*
[b] *Department of Chemistry, Imperial College of Science Technology and Medicine, South Kensington, London, UK, SW7 2AY*

**Microwave dielectric heating is rapidly becoming an established procedure in synthetic chemistry. This review summarises the basic theory underlying microwave dielectric heating and collates the dielectric data for a wide range of organic solvents which are commmonly used in microwave syntheses. The loss tangents of the solvents, which may be related to the ability of the solvent to absorb energy in a microwave cavity, depend on the relaxation times of the molecules. These relaxation times depend critically on the nature of the functional groups and the volume of the molecule. Functional groups capable of hydrogen bonding have a particularly strong influence on the relaxation times. The relaxation times of solvents decrease as the temperature of the solvent is increased. Loss tangent data at different microwave frequencies are also presented and discussed.**

*Camelia Gabriel is founder and Director of Microwave Consultants Ltd. Her main research interests are concerned with the interaction of electromagnetic radiation with materials and their application in industry. Other special interests include the biological effects of electromagnetic radiation and their implications in terms of health and the safety of people. She is active in National and European committees on safe exposure to electromagnetic fields.*

**Camelia Gabriel**

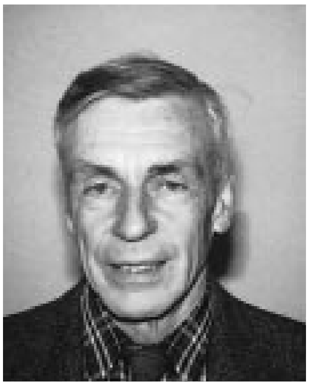
*Sami Gabriel is an engineer in the field of Electromagnetics and Information Technology. He has carried out post-graduate research at King's College London and Imperial College on the dielectric properties of organic and inorganic materials. He is involved in the development and implementation of a national materials database holding dielectric data on organic and inorganic materials. His commercial interests include the development of dielectric measurement software and field monitoring of non-ionising radiation and its implications on health and safety.*

*Edward Grant was born in Croydon in 1931 and educated at Selhurst Grammar School and King's College London. He obtained his PhD at the Middlesex Hospital Medical School where he worked on the dielectric properties of biological materials, an area in which he is still currently active. He has been Professor (now Emeritus) of Physics in the University of London since 1974 and was Head of the Physics Department at King's College just prior to retirement. He has spent 18 months at Imperial College working with Professor D. M. P. Mingos and is now Principal Scientific Consultant to Microwave Consultants Limited (MCL).*

*Ben Halstead was born in Rainham, Kent. He graduated from Hull University in 1994 and is currently researching dielectric heating effects in inorganic synthesis, at Imperial College.*

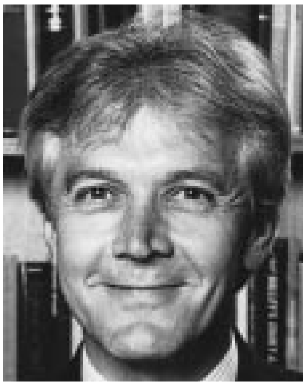
*Michael Mingos was born in Basrah, Iraq in 1944 and was an undergraduate at UMIST. After a DPhil at Sussex University he did postdoctoral work at Northwestern University. He is currently the Sir Edward Frankland BP Professor of Inorganic Chemistry at Imperial College of Science, Technology and Medicine.*

**Sami Gabriel**



**Edward H. Grant**

**Ben S. J. Halstead**



**D. Michael P. Mingos**

## 1 Introduction

Microwave dielectric heating is a well established procedure not only for the domestic preparation of meals, but also it is widely used industrially for the processing of food and industrial materials. Microwave applications have been designed for the volumetric heating of rubber, wood, paper and agricultural products and for the inclusion of waste materials into glasses.[1] The classic work of von Hippel and his co-workers[2] in the early 1950s provided a sound theoretical basis for these technological developments and his group provided an important database of dielectric properties on common substances, foodstuffs and materials.[3] This database has been expanded upon as the technological need arose and more recently a considerable effort has been directed towards the measurement of the dielectric properties of biological materials.[4,5] This was prompted in part by a need to provide fundamental data which would underpin the public and scientific discussions concerning the health hazards[6] which may arise from the interaction of electromagnetic radiation in the microwave and radio frequency ranges with biological tissues, and the widespread use of electromagnetic radiation in various medical diagnostic and therapeutic procedures. The dielectric analysis of pharmaceutical materials has increased in importance in recent years and Craig has written a timely book summarising the theoretical and practical aspects of these studies.[7]

More recently microwave dielectric heating has attracted the attention of chemists.[8] Initially the reduced time scales of chemical reactions which were performed in microwave cavities were attributed to a specific ‘microwave effect’, however more detailed reaction rate measurements have established that in general chemical reactions which occur under microwave conditions are governed by the same fundamental principles of thermodynamics and kinetics as reactions which occur under conventional conditions.[9,10] A recent *Chemical Society Review* has given a balanced acount of these developments.[11]

Microwave dielectric heating has the following advantages compared to conventional heating for chemical conversions.

(1) The introduction of microwave energy into a chemical reaction which has at least one component which is capable of coupling strongly with microwaves can lead to much higher heating rates than those which are achieved conventionally.

(2) The microwave energy is introduced into the chemical reactor remotely and therefore there is no direct contact between the energy source and the reacting chemicals. This when combined with (1) above may lead to a significantly different temperature profile for the reaction and may lead to an alternative distribution of chemical products from a reaction.

(3) Chemicals and the containment materials for chemical reactions do not interact equally with the commonly used microwave frequencies for dielectric heating and consequently selective heating may be achieved. Specifically the containment materials for a chemical reaction may be chosen in such a way that the microwave energy passes through the walls of the vessel and heats only the reactants.

The very high temperatures which result when metal powders are exposed to microwave fields have been used to create ‘hot spots’ which accelerate the reactions of the metals with gases, other inorganic solids and organic substrates.[12]

(4) These selective interactions mean that microwave dielectric heating is an ideal method for accelerating chemical reactions under increased pressure conditions. Using quite simple apparatus based either on transparent plastics, *e.g.* Teflon or glass, it is possible to increase the temperature of a reaction in common organic solvents up to 100 °C above the conventional boiling point of the solvent. For example, ethanol has a conventional boiling point of 79 °C, microwave dielectric heating in a closed vessel can rapidly lead to temperatures of 164 °C and a pressure of 12 atmospheres. This higher temperature leads to a thousand-fold acceleration of the reaction rate, for reactions which are studied in this solvent.[13]

The advantages outlined above have been exploited by chemists extensively during the last ten years and to date more than 300 papers have been published describing the applications of microwave dielectric heating to chemical problems.[14] However, much of the work has been empirical and qualitative. The theoretical basis of microwave dielectric heating remains poorly understood by many chemists and although the database of dielectric properties initiated by von Hippel and extended by others[2] contains much information about materials and foodstuffs, the data for commonly available organic solvents used for chemical reactions are not readily available to the chemical community. The recent developments in dielectric measuring techniques using wideband swept frequency instrumentation have made it relatively easy to obtain the required dielectric data in order to interpret the heating characteristics of a wide range of chemicals.[15] This review has the following specific aims:

1. To provide a basic introduction to dielectric theory which will enable chemists to understand at a molecular level the fundamental nature of the phenomenon which results in the heating of solutions in microwave fields.
2. To provide an interpretation of the relaxation times associated with the rotational behaviour of homologous series of solvents and account for their relative abilities to couple with microwave radiation.
3. To consider the consequences of having mixtures of solvents and salts dissolved in the solvents.
4. To define the relationships between the dielectric properties of the materials and their heating rates in commonly encountered situations.
5. To provide a database of dielectric parameters for organic solvents which are used in synthetic organic and inorganic chemistry.[15–17]

## 2 Fundamental theory[5,16,17]

A dielectric material is one which contains either permanent or induced dipoles which when placed between two electrodes acts as a capacitor, *i.e.* the material allows charge to be stored and no dc conductivity is observed between the plates. The polarisation of dielectrics arises from the finite displacement of charges or rotation of dipoles in an electric field and should not be confused with conduction which results from translational motion of the charges when the electric field is applied. At the molecular level polarisation involves either the distortion of the distribution of the electron cloud within a molecule or the physical rotation of molecular dipoles. The latter are particularly significant in the context of microwave dielectric heating. The permittivity of a material, $\varepsilon$, is a property which describes the charge storing ability of that substance irrespective of the sample’s dimensions. The dielectric constant or relative permittivity is the permittivity of the material relative to that of free space, and Table 1 gives some representative values. It is

**Table 1** Value of relative permittivity (dielectric constant) at 20 °C for some common solvents[a]

| Solvent | Dielectric constant ($\varepsilon_S$) |
|---|---|
| Benzene | 2.3 |
| Carbon tetrachloride | 2.2 |
| Chloroform | 4.8 |
| Acetone[b] | 21.4 |
| Ethanol[b] | 25.7 |
| Methanol[b] | 33.7 |
| Water[b] | 80.4 |

[a] Data have been taken from reference 7. [b] For those polar compounds $\varepsilon'$ is frequency dependent and the values given in the Table refer to the static value $\varepsilon_S$.

noteworthy that compounds which have large permanent dipole moments also have large dielectric constants, because the dielectric polarisation depends primarily on the ability of their dipoles to reorientate in an applied electric field. In the gas and liquid phases the molecules rotate so rapidly that they are normally able to respond to field reverses occurring at $10^6$ times a second or higher, but in the solid state the molecular rotations are generally restricted and therefore reorientation in an electric field does not generally contribute to the dielectric constant.

If the electric field component is reversed much more rapidly, *e.g.* at $10^{12}$ times per second, even the smallest molecules are no longer able to rotate a significant amount before the electric field is reversed and the permittivity necessarily falls. Such rapid field reversals are of course produced when the material is exposed to electromagnetic radiation. The permittivity of the material, is therefore frequency dependent and for a polar liquid generally shows a marked decrease as the frequency of the electromagnetic radiation increases from $10^6$ (radio frequencies) to $10^{12}$ Hz (infrared frequencies). The precise frequency at which this falls reflects the frequency of the rotations within the molecule, which in turn depends on the size of the molecule and the intermolecular forces which it experiences in solution. For polar molecules with molecular weights less than a few hundred this relaxation process occurs in the microwave region, *i.e.* in the frequency range 300 MHz–300 GHz.

The re-orientation of the dipoles and displacement of charge is equivalent to an electric currrent, known as the Maxwell displacement current and named after the author of electromagnetic theory. For an ideal dielectric there is no lag between the orientation of the molecules and the variations of the alternating voltage the displacement current is 90° out-of-phase with the oscillating electric field as shown in Fig. 1. The relevant phase diagram, shown in Fig. 2(*a*), shows that for a dielectric material where the molecules can keep pace with the field changes no heating occurs. There is no component of the current in-phase with the electric field, *i.e.* the product $E \times I$ is zero because of the 90° phase lag between the field and the current.

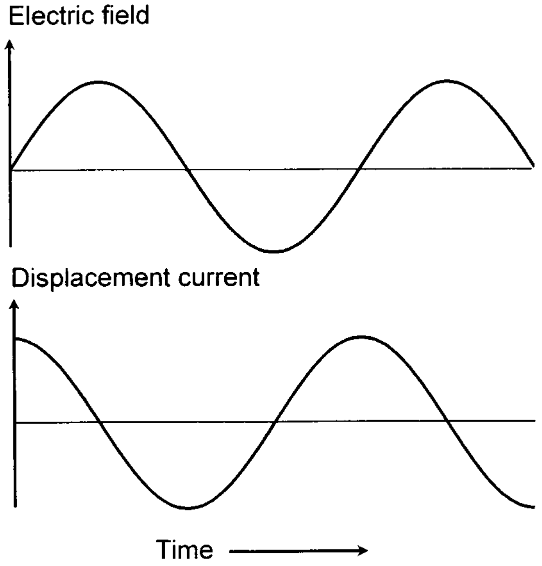


**Fig. 1** Application of a sinusoidal electric field to liquid ideal dielectric (top) and the out-of-phase diplacement current which is induced (bottom)

If the frequency of the electromagnetic radiation is pushed up into the microwave region ( ~ $10^9$ Hz) the rotations of the polar molecules in the liquid begin to lag behind the electric field oscillations. The resulting phase displacement $\delta$, shown in Fig 2(*b*) acquires a component $I \times \sin\delta$ in phase with the electric field and so resistive heating occurs in the medium—this is described as dielectric loss and causes energy to be absorbed from the electric field. Since the dipoles are unable to follow the higher frequency electric field oscillations the permittivity falls at the higher frequency and the substance behaves increasingly like a non-polar material.

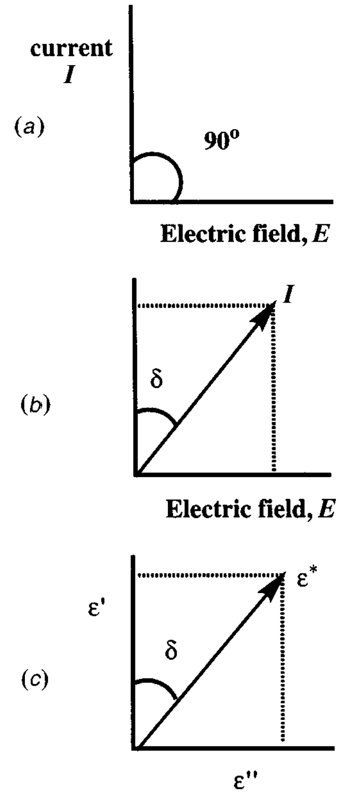


**Fig. 2** Phase diagrams for (*a*) an ideal dielectric where the energy is transmitted without loss; (*b*) where there is a phase displacement $\delta$) and the current acquires a component $I \times \sin\delta$ in-phase with the voltage and consequently there is a dissipation of energy. In (*c*) the relationship between $\varepsilon^*$, $\varepsilon'$ and $\varepsilon''$ is illustrated; $\tan\delta = \varepsilon''/\varepsilon'$.

At frequencies for which the loss angle ($\delta$) differs significantly from 90° the liquid has a dual role. It functions both as a dielectric and as a conductor. Since sinδ is an in-phase current component it gives the total relative permittivity a complex character.

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{1}$$

where $\varepsilon'$ is the real part of the relative permittivity (the dielectric constant) and $\varepsilon''$ is the loss factor which reflects the conductance of the material. In the phase diagram [Fig 2(*c*)] $\varepsilon''/\varepsilon' = \tan\delta$ and $\tan\delta$ is described as the energy dissipation factor, or loss tangent, which for low values of $\tan\delta$ provides a convenient parameter for comparing the efficiency of conversion of microwave energy into thermal energy within the dielectric for materials with comparable $\varepsilon'$. Athough $\tan\delta$ is a helpful parameter for comparing the heating rates of a series of compounds with similar chemical and physical characteristics more complex expressions, which take into account the complexity of the electric field pattern, the heat capacity of the compound and its density, are required in order to calculate these heating rates reliably.

The frequency dependence of $\varepsilon'$ and $\varepsilon''$ and their magnitudes control the extent to which a substance is able to couple with microwave radiation and are therefore fundamental parameters for interpreting the dielectric heating phenomenon.

For a polar liquid with a single relaxation time the complex permittivity can be expressed by the following equation due to Debye

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \tag{2}$$

where $\tau$ is the relaxation time and $\varepsilon_s$ and $\varepsilon_\infty$ are the values of permittivity at frequencies $\ll \tau^{-1}$ and $\gg \tau^{-1}$ respectively.

Using Eqn (1) and separating into real and imaginary parts leads to

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+\omega^2\tau^2} \quad (3)$$

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1+\omega^2\tau^2} \quad (4)$$

The relaxation time, $\tau$, has the following significance. The application of a static electric field to a solution containing polar molecules will have the effect of aligning the molecules in the direction of the external field. If the field is switched off the molecules do not immediately adopt random orientations. The relaxation time is a measure of the time taken to achieve this randomised state.

The maximum value of $\varepsilon''$ occurs when $\varepsilon'$ reaches half of its declining value between $\varepsilon_s$ (the permittivity in a static field) and $\varepsilon_\infty$ (the permittivity at frequencies much greater than the inverse of $\tau$). The angular frequency of the electromagnetic radiation $\omega = 2\pi\nu$ and $\tau = 1/\omega_o$, where $\omega_o$ is the angular frequency at which $\varepsilon''$ is a maximum. The maximum in $\tan\delta$ occurs at slightly higher frequencies than the maximum in $\varepsilon''$ since $\varepsilon''/\varepsilon' = \tan\delta$.

For a spherical molecule of radius $r$ rotating in a viscous continuum the relaxation time may be interpreted using the following expression, also due to Debye

$$\tau = 4\pi r^3\eta/kT \quad (5)$$

which emphasises the importance of the volume of the molecule $4/3\pi r^3$ and the viscosity, $\eta$, of the medium. The latter, like the relaxation time, is strongly related to the intermolecular forces. For example, when liquid water freezes the loss of rotational freedom has a dramatic effect on the relaxation time, increasing it by approximately $10^6$.

The relaxation time is temperature dependent and since it is related to the rate constant, $k$, for the relaxation process an Arrhenius type analysis may be used to calculate the enthalpy and entropy of the relaxation process. For liquid water $\Delta H^\ddagger$ (enthalpy of activation) is 18 kJ mol$^{-1}$ which corresponds roughly to the energy required to break one hydrogen bond. For ice the equivalent value is 55 kJ mol$^{-1}$ thereby suggesting that three hydrogen bonds are involved. Since the water molecules in ice form four hydrogen bonds with neighbouring molecules this observation is consistent with what would be expected for a rotation process which retains one hydrogen bond. The water molecules in liquid water clearly retain some of the structure of ice and it is perhaps better to think of water either as a series of clusters of water molecules which interact with each other or as a statistical assembly of water molecules forming different numbers of hydrogen bonds. As a consequence of the former the relaxation process in the microwave region corresponds to cooperative rotational movements of molecules within the clusters and between the clusters. Whereas in the latter it is an average relaxation time resulting from the different bonding arrangements adopted in the liquid.

It should be emphasised that the interaction between the microwave radiation and the polar solvent which occurs when the frequency of the radiation approximately matches the frequency of the rotational relaxation processes is not a quantum mechanical resonance phenomenon. Transitions between quantised rotational bands are not involved and the energy transfer is not a property of a specific molecule, but the result of a collective phenomenon involving the bulk. In the Debye interpretation the heat is generated by frictional forces occurring between the polar molecule, whose rotational velocity has been increased by the coupling with the microwave radiation, and neighbouring molecules. A more chemical view of the process would involve the increase in the translational energy of neighbouring molecules induced by the more rapid rotation of the central molecule, which acts like a bat or paddle knocking away neighbouring molecules as a result of its faster rotation.

In the liquid phase the molecules experience many different environments both spatially and as a function of time but mathematically the dispersion can often be expressed in terms of a single average relaxation time (Eqns. 2 and 3 ). However, the dispersion region is spread out over at least two decades and consequently dielectric heating is a broad band phenomenon and rapid energy transfer occurs even when the frequency of the microwaves and the relaxation frequency are not perfectly matched.

Studies on the relaxation properties of mixtures of solvents have provided some interesting insights into the volumes implicated by the Debye expression and the nature of the mixing process. If the solvents are chemically similar and mix well at the molecular level then the mixture will often exhibit a single relaxation time at an average position which reflects the molar ratios of the two components. However, if the solvents do not mix well at the molecular level, *e.g.* alcohols and bromides and alcohols and ethers, then two distinct relaxation times are observed and they do not differ greatly from those of the pure solvents. This suggests that the molecules do not experience average environments, but form aggregates which are micro-assemblies of like molecules. Therefore, the relaxation times resemble those of the pure solvents and the relaxation volumes are significantly larger than the molecular volumes, indicating that the relaxation processes are occurring within an aggregate of molecules.[17]

## 3 Aqueous systems

The dielectric properties of water and aqueous solutions are clearly relevant to the primary applications of microwave dielectric heating in domestic and commericial applications and consequently the available data and their interpretation are reasonably well documented. In this section a brief survey will be given of the dielectric properties of water and aqueous solutions, including biological materials. The subject has been treated comprehensively recently by Craig.[7]

The permittivity/frequency graph for pure water at 20 °C is illustrated in Fig. 3 and the graphs are well reproduced using Eqns. (2) and (3). At 20 °C the relaxation time for water is $9 \times 10^{12}$ s, *i.e.* it has a relaxation frequency of *ca.* 18 GHz. Therefore, the most effective conversion of microwave energy into thermal energy will occur in this frequency region. In practice the majority of commercial and domestic microwave appliances function at 2.45 GHz (this corresponds to a relaxation time of 65 ps), which is displaced from this maximum and the implications of this difference are discussed further below.

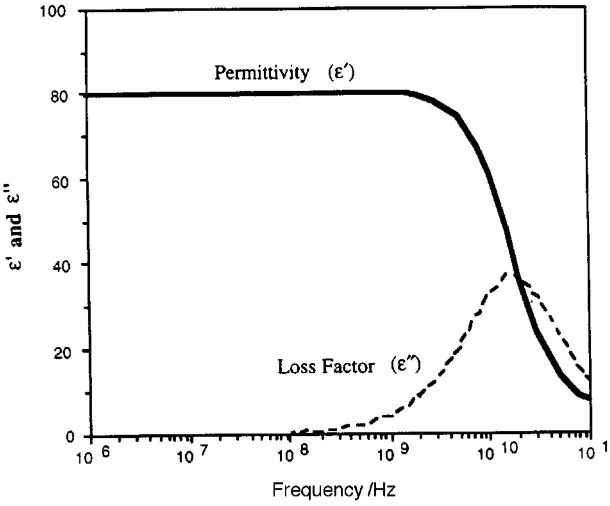


**Fig. 3** The variation of $\varepsilon'$ and $\varepsilon''$ with frequency for water at 20 °C

The structure of water is influenced when ionic salts are dissolved in it and the relaxation time decreases at low concentrations and then increases. It has been proposed that the presence of the ions causes a structure breaking process to occur in water. Those water molecules which are coordinated to the ions are rotationally fixed, but those which are not coordinated do not experience such strong intermolecular hydrogen bonding effects and consequently in this freer state they have lower relaxation times.[7]

At higher concentrations the effects are reversed and the relaxation frequency of water in concentrated salt solutions is higher than that of pure water, presumably due to a greater ordering of the water molecules when a large number of ions are present.

At frequencies in excess of around 100 GHz contributions from resonance absorption due to intermolecular vibrations are observed.[19] This extra dispersion region explains why, for water, the permittivity at the high frequency limit of the Debye dispersion is greater than that at optical frequencies.

### 3.1 Water–alcohol and water–carbohydrates mixtures

Alcohols and carbohydrates are likely to be highly miscible with water and may be viewed as organic radicals with pendant hydroxy groups and in solution their molecules are able to form intermolecular hydrogen bonds with each other or with neighbouring water molecules. They form an interactive mixture characterised by a main dispersion with parameters that vary continuously between those of the components.[20] The dispersion may, however, be broader than that predicted by the Debye expression and may be better described by, for example:

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\omega\tau)^{(1-\alpha)}} \tag{6}$$

This equation is empirical in its derivation and is known as the Cole–Cole model in which $\alpha$ is a distribution parameter acting on the relaxation time such that $1 > \alpha \geqslant 0$ which for $\alpha = 0$ reverts to the Debye equation. Implicit in this analysis of interactive mixtures is the fact that some of the water in the system is affected by the presence of the organic molecule and may well be referred to as bound water. The broadening of the dispersion is, however, mathematically equivalent to multiple Debye dispersions spanning a distribution of relaxation times.

Another model which is useful for describing the frequency dependence of some sugars and alcohols is due to Davidson and Cole[21] and is given by

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\omega\tau)^{\beta}} \tag{7}$$

which for $\beta = 1$ reverts to the Debye equation. The Cole–Davidson model is useful for describing those situations where a skewed distribution of relaxation times is present.

### 3.2 Aqueous protein solution[5]

A protein molecule typically has a molecular weight several orders of magnitude greater than that of water. Consequently the dielectric dispersion region for a protein occurs at frequencies well below those observed for pure water. For a moderate sized globular protein, such as haemoglobin, the relaxation frequency is in the 1–10 MHz region as distinct from around 20 GHz for the water component (Fig. 4). For low protein concentrations the bulk of the water will be relatively unaffected by the presence of the protein and two well defined dispersion regions are observed.[22–25] In Fig. 4 the water relaxation region is shown as the $\gamma$ dispersion and that of the protein the $\beta$ dispersion according to convention. At higher concentrations a significant amount of the water is influenced by the protein and is described as bound water. Because of the stronger intermolecular forces arising from the influence of the protein, bound water exhibits its dielectric dispersion at frequencies less than free water; typically an order of magnitude is involved. The bound water dispersion occurs as a small extra dispersion between the $\beta$ and $\gamma$ dispersions.

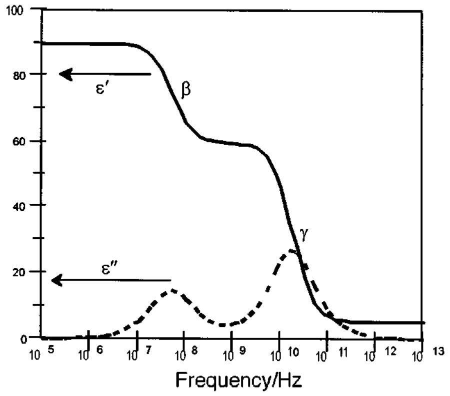


**Fig. 4** Schematic illustration of the dielectric spectrum of an aqueous protein solution

Grant *et al.*[5] have established a linear relationship between the relaxation time of water and the molecular weight of 20 biological molecules with molecular weights up to 68 000 (haemoglobin), which suggests that the size of the molecule is the predominant influence.

### 3.3 Ionic solutions

The dielectric properties of ionic solutions have been described by Hasted[26] and Craig.[7] A typical example is shown in Fig. 5, where the dielectric dispersion curves for three concentrations of potassium chloride in water are shown. For an aqueous solution of ions there are two processes leading to energy absorption and therefore dielectric heating. These are ionic drift which gives rise to Joule heating and dipolar relaxation due to the relaxation of the water molecules. The conductivity of these loss processes may be represented by $\sigma_i$ and $\sigma_d$ respectively, and the correspondiing loss factors are $\varepsilon_i''$ and $\varepsilon_d''$. The relationship between $\varepsilon''$ and $\sigma$ is:

$$\varepsilon'' = \sigma/\omega\varepsilon_0 = (\sigma_d + \sigma_i)/\omega\varepsilon_0 \tag{8}$$

and consequently Eqn. (1) may be written

$$\varepsilon^* = \varepsilon' - j'(\varepsilon''_d + \sigma_i/\omega\varepsilon_0) \tag{9}$$

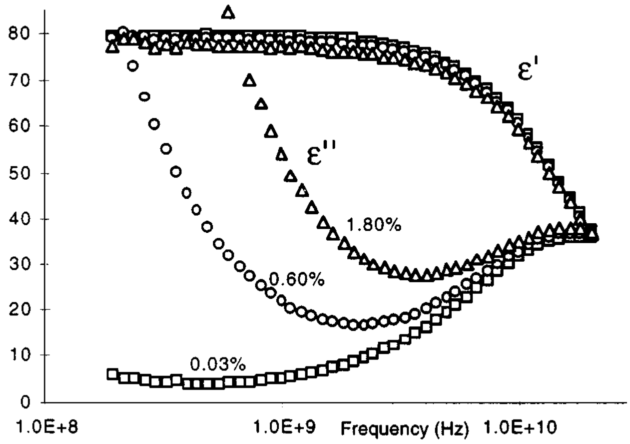


**Fig. 5** Experimental values of the permittivity and total loss factor for KCl solutions with differing concentrations

As the concentration increases the contribution of $\varepsilon_i''$ predominates over $e''_d$ and consequently the value of $\varepsilon''$ increases with decreasing frequency (Fig. 5). From a chemical point of view this means that the introduction of ions into a solution leads to a marked increase in dielectric heating rates.

### 3.4 Organic compounds

Although the relaxation times of a range of organic molecules have been discussed at some length[16,17] the dielectric properties at frequencies which are relevant to microwave dielectric heating are less available. In this review we have collected together these data. In addition the dielectric data for a wide range of organic compounds which are of interest as potential solvents for microwave dielectric heating have been remeasured recently in our laboratories[15] and the important features of the data are discussed below. The dielectric properties of the compounds were measured at a range of frequencies from 300 kHz to 20 GHz and at a fixed temperature of 20 °C. The temperature dependence of the dielectric properties of many of the compounds were also measured and are discussed below. The static permittivity and the relaxation times were obtained by curve fitting the experimental data to the Cole–Cole model [Eqn. (6)] with, $\varepsilon_\infty = 3$, this being the average value for the compounds studied. In fact the fitted values of $\varepsilon_s$ and $\tau$ are not particularly sensitive to the value of $\varepsilon_\infty$. The analysis also showed that $\alpha \rightarrow 0$ *i.e.* the dielectric behaviour of the compounds was represented to a good approximation by the Debye Eqns. (3) and (4).

### 3.5 Alcohols

Alcohols are able to form hydrogen bonds in much the same way as water, albeit to a lesser extent and therefore their dielectric properties bear many similarities to those of water. The aliphatic alcohols also have dipole moments which are similar to those of water. Table 2 summarises the relaxation times of alcohols as a function of chain length and isomer type. As the chain length of the alcohols increases the relaxation time becomes longer. The results fit in well with those anticipated from the Debye expression [Eqn. (5)] and Fig. 6 shows an approximately linear relationship between the relaxation time and the product of the calculated molecular volume and the viscosity. Therefore, it can be reasonably assumed that with the exception of benzyl alcohol it is the restricted rotation of the whole molecule which is giving rise to the relaxation process which occurs in the microwave region. The data in Table 2 also suggest that the relaxation time is not greatly influenced by the position of the OH group in the molecule since isomeric alcohols, *e.g.* the isomeric propanols and butanols have similar relaxation times. The data in Table 2 do, however, indicate a significant decrease in the relaxation times when the hydrocarbon chain contains a double bond or a phenyl ring adjacent to the $CH_2OH$ fragment. It is possible that in these more rigid molecules a more localised rotational process is being observed at these frequencies and this aspect is discussed in more detail below.

**Table 2** Relaxation times (at 20 °C) and dielectric properties of aliphatic alcohols compared with $H_2O$

| Compound | Relaxation time $\tau$ /ps | Dipole moment Debye | Viscosity millipoise | Loss tangent at 2.45 GHz |
|---|---|---|---|---|
| $H_2O$[a] | 9.04 | 1.84 | 10.1 | 0.123 |
| MeOH | 51.5 | 1.70 | 5.45 | 0.659 |
| EtOH | 170 | 1.69 | 10.8 | 0.941 |
| Propan-1-ol | 332 | 1.68 | 20 | 0.757 |
| Propan-2-ol | 237 | 1.66 | 17.7 | 0.799 |
| Butan-1-ol | 538 | 1.66 | 22.7 | 0.571 |
| Butan-2-ol | 562 | | | 0.447 |
| 2-Methylpropan-1-ol | 644 | | | 0.522 |
| Pentan-1-ol | 792 | 1.80 | 33.5 | 0.427 |
| Hexan-1-ol | 976 | 1.67 | | 0.344 |
| Pent-4-en-1-ol | 322 | | | 0.669 |
| Pent-3-en-2-ol | 169 | | | 0.720 |
| 3-Methyl but-2-en-1-ol | 170 | | | 0.846 |
| *trans*-Hex-2-en-1-ol | 277 | | | 0.571 |
| Benzyl alcohol | 188 | | | 0.667 |

[a] 1.84 refers to the dipole moment in the vapour phase—in the liquid state it is appreciably higher (*ca.* 2.5 D).

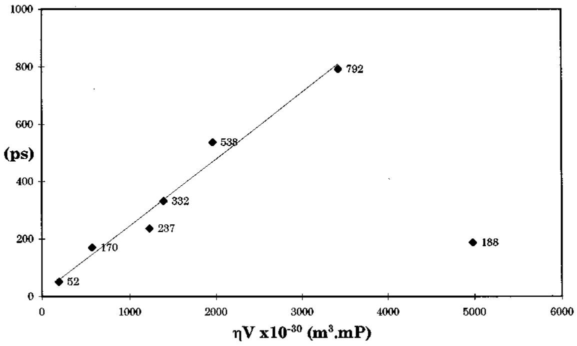


**Fig. 6** Plot of relaxation time $\tau$ *vs* $4/3\pi r^3$ for a number of alcohols. The specific points may be identified by their relaxations times which are given in Table 2. The anomalous position of the point for benzyl alcohol is particularly noteworthy.

The slope of the line in Fig. 6 gives $\tau/V\eta = 2.4 \times 10^{-21}$ J$^{-1}$. For a rigid sphere rotating in a continuum the slope should be $3/kT$ which at 20 °C is equal to $0.74 \times 10^{-21}$ J$^{-1}$ according to the Debye Eqn. (5), which highlights the limitations of the Debye analysis and the assumption that molecules behave as rigid hard spheres. There have been a number of attempts to build into the Debye equation parameters which take into account the varying shapes of molecules, their tendency to aggregate and the directional nature of hydrogen bonding interactions.[5,17]

Although, the relaxation times are important in influencing heating rates the breadth of the $\varepsilon''$ against frequency curves is also important and Fig. 7 illustrates the dielectric spectra for water and aliphatic alcohols in the range $10^8$–$10^{11}$ Hz. The value of the dielectric increment ($\varepsilon_s - \varepsilon_\infty$) is related by the Kirkwood equation[28] to the correlation factor $g$ which takes into account the highly directional nature of the hydrogen bonds, the dipole moment of the molecule ($\mu$) and the number of molecules in a unit volume ($n$).

$$\varepsilon_s = \varepsilon_\infty + \frac{gn\mu^2}{2\varepsilon_0 kT} \qquad (10)$$

For water the $g$ parameter expression is around 2.5 and increases as the chain length increases. Some representative values are given in Table 3. As the molecules become more complex the complexity of the rotational relaxation increases and the permittivity-curves reflect the superposition of an increasing number of relaxation processes within the molecules and between molecules as a result of self association.

**Table 3** Values of static permittivity ($\varepsilon_S$) and Kirkwood correlation factor $g$ for some non-aqueous solvents.[a]

| | $T$/°C | $\varepsilon_S$ | $g$ |
|---|---|---|---|
| MeOH | 20 | 32.8 | 2.94 |
| EtOH | 20 | 24.6 | 3.04 |
| Propan-1-ol | 20 | 19.5 | 3.07 |
| Pentan-1-ol | 20 | 15.8 | 3.43 |

[a] See also reference 7, page 60.

The standard microwave frequency for dielectric heating of 2.45 GHz corresponds to a relaxation time of 65 ps. Therefore, the alcohols listed in Table 2, which have relaxation times of 51.5–800 ps, have relaxation properties which enable them to couple effectively with this fixed microwave frequency and have therefore proved to be effective solvents for dielectric heating.[14] The loss tangents given in Table 2 for alcohols are in fact significantly larger than that of water itself. The more detailed relationships between loss tangents and heating rates will be discussed in a subsequent section.

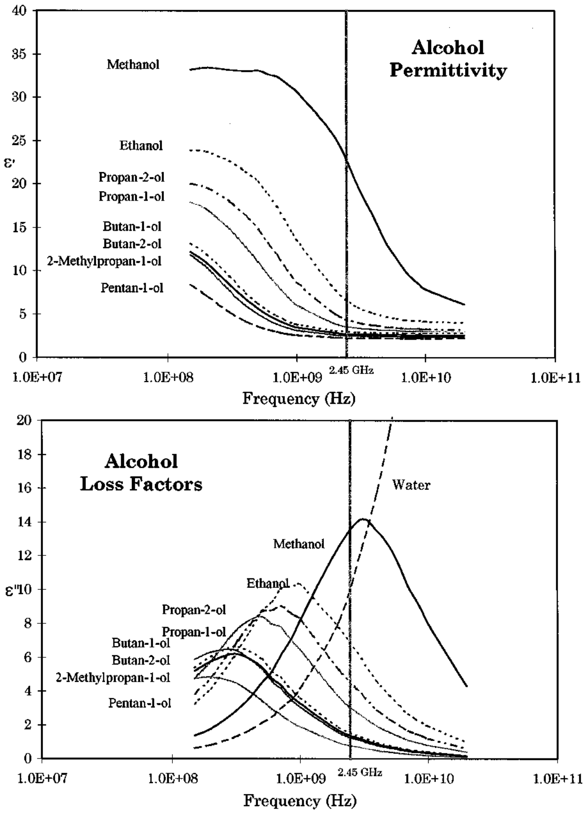


**Fig. 7** Dielectric spectra for water and a range of alcohols

## 4 Nitriles, esters, ketones and chlorohydrocarbons

The relaxation times for a series of nitriles are given in Table 4 together with some of the relevant loss tangents at 2.45 GHz. The weaker hydrogen bonding in these compounds leads to much shorter relaxation times (4–68 ps) and for the earlier members of the homologous series much smaller loss tangents than the aliphatic alcohols discussed previously. The relaxation times of the nitriles are much less sensitive to the increase in the hydrocarbon chain length than those noted above for alcohols. Presumably, the increased volume and the viscosity have a cancelling effect. The loss tangents for the more commonly used nitriles are comparable with water and therefore the aliphatic nitriles may be used effectively as solvents in microwave cavities. The relaxation time for benzonitrile, a common solvent for coordination and organometallic chemistry more closely matches that of the fixed frequency microwave source commonly used in cavities and this is reflected in the larger loss tangent. The loss tangents of the longer chain nitriles are similar to that for benzonitrile.

The relaxation times given in Table 4 for some esters and ketones are similar to those for nitriles and clearly indicate the absence of strong hydrogen bonding and the importance of increasing molecular volume. The halogeneated aliphatic compounds listed in Table 4 also exhibit similar and short relaxation times (4–15 ps). It is noteworthy that the relaxation times for these molecules are almost independent of the halogen and occur in a relatively narrow range. Tetrahydrofuran and nitromethane have relatively short relaxation times, but the relaxation time for DMF is comparable to those for nitriles. Formic acid and acetic acid have long relaxation times, because of the strong hydrogen bonding associated with the carboxylic acid groups and the large loss tangent of formic acid at 2.45 GHz is particularly noteworthy.

## 5 Aromatic compounds

Table 5 summarises the relaxation times and loss tangents of a series of mono-substituted benzene derivatives. The chloro-, bromo- and iodo-derivatives have very similar dipole moments and the relaxation time increases progressively as the volume of the substituent increases. The relaxation times of nitrobenzene and benzonitrile are longer and their loss tangents suggest that

**Table 4** Relaxation times of some nitriles, esters, carboxylic acids, ketones and chlorohydrocarbons. (Literature data in italics)

| Compound | Relaxation time, $\tau$/ps | Loss tangent at 2.45 GHz | Ref. |
|---|---|---|---|
| Nitriles | | | |
| $CH_3CN$ | 4.47 (20 °C) | 0.062 | |
| | *3.21 (25 °C)* | *0.052* | [a] |
| | *3.4 (25 °C)* | *0.049* | [b] |
| $CH_2{=}CHCN$ | 5.91 (20 °C) | 0.082 | |
| $CH_3CH{=}CHCN$ | 10.8 (20 °C) | 0.149 | |
| $CH_3CH_2CH_2CN$ | *8.9 (25 °C)* | *0.119* | [b] |
| $(CH_3)_2CHCN$ | 7.92 (20 °C) | 0.107 | |
| $CH_3(CH_2)_3CN$ | 12.9 (20 °C) | 0.167 | |
| | *13.0 (25 °C)* | *0.172* | [b] |
| $CH_3(CH_2)_4CN$ | *17.4 (25 °C)* | *0.215* | [b] |
| $CH_3(CH_2)_6CN$ | *31.4 (25 °C)* | *0.343* | [b] |
| $CH_3(CH_2)_8CN$ | *67.5 (25 °C)* | *0.527* | [b] |
| $CH_3(CH_2)_9CN$ | *64.6 (25 °C)* | *0.500* | [b] |
| PhCN | 33.5 (20 °C) | 0.459 | |
| Esters | | | |
| $CH_3CO_2Et$ | 4.41 (20 °C) | 0.059 | |
| | *3.66 (40 °C)* | | [c] |
| $CH_3CO_2C_{16}H_{31}$ | *13.3 (35 °C)* | | [c] |
| $C_{17}H_{35}CO_2C_{10}H_{21}$ | *30.8 (40 °C)* | | [c] |
| Acids | | | |
| $HCO_2H$ | *76.7 (25 °C)* | *0.722* | [d] |
| $CH_3CO_2H$ | *177.4 (25 °C)* | *0.174* | [d] |
| Ketones | | | |
| $CH_3COCH_3$ | 3.54 (20 °C) | 0.054 | |
| | *3.22 (20 °C)* | *0.045* | [e] |
| | *3.40 (25 °C)* | *0.045* | [f] |
| $CH_3COCH_2CH_3$ | 5.90 (20 °C) | 0.079 | |
| $(CH_3)_2CHCOCH_2CH_3$ | 11.3 (20 °C) | 0.143 | |
| Chlorinated hydrocarbons | | | |
| $CHCl_3$ | 8.94 (20 °C) | 0.091 | |
| | *7.20 (25 °C)* | *0.058* | [g] |
| $CH_2Cl_2$ | 3.12 (20 °C) | 0.042 | |
| | *2.07 (20 °C)* | *0.027* | [h] |
| $CH_2ClCH_2Cl$ | 11.14 (20 °C) | 0.127 | |
| $CHCl_2CH_2Cl$ | 15.18 (20 °C) | 0.181 | |
| $CH_3CCl_3$ | *5.9 (20 °C)* | | [c] |
| $(CH_3)_2CCl_2$ | *6.4 (20 °C)* | | [c] |
| $(CH_3)_3CCl$ | *4.8 (20 °C)* | | [c] |
| $(CH)_3CBr$ | *6.7 (20 °C)* | | [c] |
| thf, $C_4H_8O$ | 3.49 (20 °C) | 0.047 | |
| | *4.0 (25 °C)* | *0.030* | [f] |
| $CH_3NO_2$ | 4.51 (20 °C) | 0.064 | |
| $HCONH_2$ | *37.3 (25 °C)* | *0.561* | [a] |
| | *38.3 (25 °C)* | *0.524* | [i] |
| $HCONH(CH_3)$ | *128 (25 °C)* | | [a] |
| | *122.9 (25 °C)* | *1.610* | [i] |
| $HCON(CH_3)_2$ | 13.05 (20 °C) | 0.161 | |
| | *10.2 (25 °C)* | *0.142* | [i] |
| $(CH_3)_2SO$ | *20.5 (25 °C)* | *0.825* | [a] |
| | *23.1 (25 °C)* | | [j] |

[a] D. Bertolini, M. Cassetori, G. Salvetti, E. Tombarit and S. Veronesi, *Rev. Sci. Instrum.*, 1990, **61**, 450. [b] S. N. Helambe, M. P. Lokhande, A. C. Kumbharkhane and S. C. Mehrotra, *Pramana*, 1995, **45**, 19. [c] See refs. 16, 17 and also C. Clemett and M. Davies, *Trans. Farad. Soc.*, 1962, **58**, 1705. [d] U. Kaatze, K. Menzel and R. Pottel, *J. Phys. Chem.*, 1991, **95**, 324. [e] J. K. Vij, T. Grochulski, A. Kocot and F.Hufnagel, *Mol. Phys.*, 1991, **72**, 353. [f] A. C. Kumbharkhane, S. N. Helambe, M. P. Lokhande, S. Doraiswamy and S. C. Mehrotra, *Pramana*, 1996, **46**, 91. [g] J. Goulon, J. L. Rival, J. W. F. Gleming, J. Chamberlain and G. W. Chantry, *Chem. Phys. Lett.*, 1973, **18**, 211. [h] J. K. Vij, F. Hufnagel and T. Grochulksi, *J. Mol. Liq.*, 1991, **49**, 1. [i] S. M. Puranik, A. C. Kumbharkhane and S. C. Mehrotra, *Ind. J. Chem. A*, 1993, **32**, 613. [j] U. Kaatze and V. Lünnecke-Gabel, *J. Mol. Liq.*, 1991, **48**, 45.

**Table 5** Relaxation times and dielectric properties of simple aromatic compounds

| Compound | Relaxation time, $\tau$/ps | Loss tangent at 2.45 GHz | Dipole moment Debye |
|---|---|---|---|
| Chlorobenzene | 12.9 | 0.101 | 1.69 |
| Bromobenzene | 18.0 | 0.138 | 1.70 |
| Iodobenzene | 27.3 | 0.157 | 1.70 |
| Nitrobenzene | 43.7 | 0.589 | 4.22 |
| Benzonitrile | 33.5 | 0.459 | 4.68 |
| Benzaldehyde | 25.8 | 0.337 | 2.84 |

they are very effective solvents for microwave dielectric heating at the commonly used frequency. The intermolecular forces between molecules containing these substituents are probably larger because of the larger dipole moments associated with them and this is probably the primary reason for the longer relaxation times.

## 6 Polyalcohols[20]

Table 6 provides some comparative data on a series of alcohols which have several OH groups attached to the carbon backbone. These compounds are able to hydrogen bond very extensively and this is reflected in their very high viscosities, which in turn correlate with a long relaxation time. The high loss tangents associated with these solvents are particularly noteworthy and it is surprising that they have not been more widely used as solvents for synthetic procedures based on microwave dielectric heating.

It was previously noted that the activation energy for the relaxation process in water was around 15–20 kJ mol$^{-1}$. For simple aliphatic alcohols the corresponding value is in the range 16–23 kJ mol$^{-1}$ and in these polyalcohols where the extent of hydrogen bonding is very extensive and their viscosities are high then it rises to 50–130 kJ mol$^{-1}$.

## 7 Intramolecular rotations

Although the relaxation process in the microwave region is generally associated with rotation of the whole molecule there are some important exceptions. From the analysis above it is clear that as the molecular mass of the compound becomes larger as the relaxation time increases, and particularly for those solvents where hydrogen bonding is significant. However, for large relatively rigid molecules with pendant substituents it is possible to observe more localised rotational processes. A functional group, *e.g.* OH or $NH_2$, attached to a large molecule behaves as if it were anchored to an immobile raft and its localised rotations may be observed in the microwave region. For example, triphenylchloromethane and triphenylhydroxymethane have very different relaxation frequencies and it has been proposed that in the latter case the relaxation time of 10 ps is associated with a rotation of the O–H bond relative to the triphenylmethyl fragment (Fig. 8). In many compounds containing rigid phenyl groups bond rotations are observed, *e.g.* benzyl alcohol has a relaxation time of only 188 ps, whereas its molecular volume would suggest a relaxation time for complete molecular rotation of more than 1000 ps. The anomalous behaviour of benzylalcohol compared to other alcohols is clearly visible in Fig. 6. Davies and Meakins[17] were able to discern simultaneously the localised and molecular rotations in tri-*tert*-butylphenol (in decalin) and the relevant dielectric spectrum is illustrated in Fig. 9.

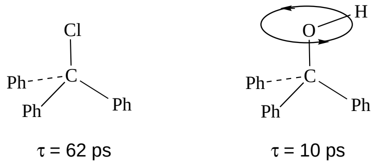


**Fig. 8** Possible localised relaxation process for $Ph_3COH$

It is signifcant from the data in Table 2 that those compounds with $CH_2OH$ groups adjacent to either a double bond or a phenyl ring have relaxation times of 170–270 ps which suggests a localised rotation of the $CH_2OH$ group. The very different relaxation frequencies of the isomeric pentenols are particularly noteworthy in this regard.

Primary amines anchored to large molecules also show relaxation frequencies which are inconsistent with the rotation of the whole molecule and it has been proposed that it is not a local rotation but an inversion at the nitrogen atom which is responsible. Table 7 summarises the data on three amines. The series of *ortho*-, *meta*- and *para*-methoxy amino-benzenes is particularly interesting since they all show a relaxation time of 25–30 ps which can be associated with inversion of the $NH_2$ groups, but the *ortho*-isomer shows in addition a second and longer relaxation process at 105 ps, which presumably is associated with the occurrence of intramolecular hydrogen bonding between the $NH_2$ and the methoxy group.

It is tempting for a chemist to give a chemical significance to these localised rotations and speculate that microwave dielectric heating of molecules containing these groups may result in an enhancement of reaction rates specifically at these groups. However, it should be recalled that the dielectric heating

**Table 6** Relaxation times and dielectric properties of glycols

| Compound | Relaxation time $\tau$/ps | Loss tangent at 2.45 GHz | Viscosity/ millipoise | Ref. |
|---|---|---|---|---|
| Ethanol | 170 | 1.26 | 10.8 | |
| Ethyleneglycol | 112.87 | 1.35 | 1.36 | |
| | *104.6 (25 °C)* | *1.17* | | [a] |
| 1,3-Propanediol | *340 (25 °C)* | *1.30* | | [b] |
| 1,4-Butanediol | *760* | *0.783* | | [b] |
| 1,5-pentanediol | *1150* | *0.456* | | [b] |
| 1,7-Heptanediol | *1950* | *0.206* | | [b] |
| 2-Methoxyethanol | 33.55 | 0.410 | | |
| | *23.7 (35 °C)* | *0.282* | | [c] |
| 2-Ethoxyethanol | *31.6 (35 °C)* | *0.301* | | [c] |
| 2-Butoxyethanol | *36.6 (35 °C)* | *0.276* | | [c] |
| Glycerol | 1215.6 | 0.651 | 9450 | |
| Di(ethylene glycol) methyl ether | *26.1 (35 °C)* | *0.310* | | [c] |
| Di(ethylene glycol) ethyl ether | *35.5 (35 °C)* | *0.325* | | [c] |
| Di(ethylene glycol) butyl ether | *43.6 (35 °C)* | *0.303* | | [c] |

[a] A. C. Kumbharkhane, S. M. Puranik and S. C. Mehrotra, *J. Sol. Chem.*, 1991, **21**, 201. [b] F. Wang, R. Pottel and U. Kaatze, *J. Phys. Chem.*, 1997, **101**, 922. [c] H. D. Purohit and R. J. Sengwa, *J. Mol. Liq.*, 1990, **47**, 53.

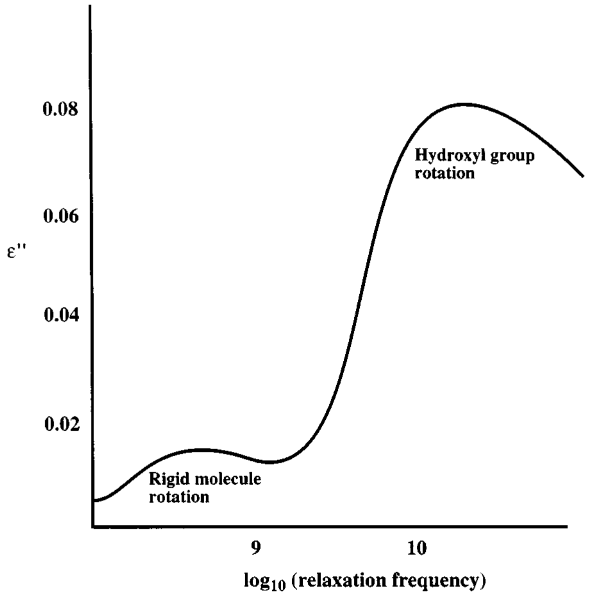


**Fig. 9** Dielectric absorption of tri-*tert*-butylphenol in decalin ( 0.76 M) at 20 °C (adapted from M. Davies and R. Meakins, *J. Chem. Phys.*, 1957, **26**, 1584).

**Table 7** Structure and dielectric parameters of three methoxybenzylamines

| | $\varepsilon_S$ | Relaxation time/ps |
|---|---|---|
| *p*-Methoxy | 7.2 | 25.4 |
| *o*-Methoxy | 7.2 | 28.1 and 105 |
| *m*-Methoxy | 7.4 | 29.2 |

process involves the rapid energy transfer from these groups to neighbouring molecules and it is not possible to store the energy in a specific part of the molecule.

## 8 More specific aspects of microwave dielectric heating

The previous section has qualitatively alluded to the relationship between the dielectric heating rates and tan$\delta$ and this section attempts to define these realationships more precisely. An excellent detailed account of this aspect has been given in the book by Metaxas and Meredith,[29] and more recent developments have been documented by Dibben and Metaxas.[30] The efficiency of conversion of microwave energy into thermal energy depends upon both the dielectric and thermal properties of the material. The fundamental relationship is

$$P = \sigma|E|^2 = (\omega\varepsilon_0\varepsilon'')|E|^2 \tag{11}$$

$$= (\omega\varepsilon_0\varepsilon' \tan\delta)|E|^2 \tag{12}$$

where $P$ stands for power dissipation per unit volume in a material of conductivity $\sigma$. The electric field in the sample is $E$ and $\omega$ is the angular frequency. Substituting for the conductivity from eqns (4) and (8) gives $P$ in terms of the Debye parameters as

$$P = \frac{\varepsilon_0(\varepsilon_s - \varepsilon_\infty)\omega^2\tau}{1+\omega^2\tau^2}|E|^2 \tag{13}$$

Assuming negligible heat loss and diffusion, the rate of heating or temperature rise $\Delta T$ in a time interval $t$ can be expressed as

$$\frac{\Delta T}{t} = \frac{\sigma|E|^2}{\rho C}$$

$$\frac{\Delta T}{t} = \frac{\omega\varepsilon_0\varepsilon''|E|^2}{\rho C} = \frac{\omega\varepsilon_0\varepsilon'\tan\delta|E|^2}{\rho C} \tag{14}$$

where $\rho$ is the density and $C$ the specific heat capacity.

In practice, the field strength is dictated by the characteristic shape and dimensions of the cavity, and the field strength in the material is neither known nor constant. Moreover the value of $E$ is itself strongly dependent upon the dielectric properties of the material. Therefore a rigorous numerical analysis is necessary in order to establish the distribution of electric field in the cavity and within the sample. This situation has been dealt with by Dibben and Metaxas.[30]

In summary, the following general points may be made:

1. Non-polar solvents, which have no permanent dipole moment have no relaxation processes in the microwave region and are therefore transparent to microwaves. Whilst, this means that they are ineffective as solvents for microwave dielectric heating experiments they may be used as coolants for removing excess heat from a microwave cavity.

2. Polar solvents, which have a permanent dipole moment, do have relaxation processes in the microwave region and are therefore suitable candidates as solvents for microwave dielectric heating experiments. The data provided in previous sections have given some guidance concerning their relaxation times and loss tangents. It is perhaps worth re-emphasising that even when the relaxation time is one or two orders of magnitude different from that which corresponds to the microwave frequency operating in the cavity then the solvent is still capable of acting as an effective medium for dielectric heating because its loss tangent is sufficiently large. Indeed the loss tangent of water at 2.45 GHz is only 0.1 and yet the heating rates are sufficiently high for this frequency to be used as the basis of an enormous food processing industry. Therefore solvents with tanδ greater than 0.1 are good bets for microwave dielectric heating experiments.

3. The relaxation time of a solvent depends on the temperature and decreases as the temperature is increased, *i.e.* the larger translational motions of the molecules enable them to randomise their position more quickly when the electric field is switched off. Therefore, if an organic solvent has a relaxation time greater than around 65 ps (*i.e.* corresponding to 2.45 GHz) it will have a loss tangent which increases with temperature. Therefore, as the temperature increases as a result of microwave dielectric heating then the loss tangent increases and the solvent converts more of the microwave energy into thermal energy. The heating rate therefore rises. The resulting phenomenon is described as thermal runaway. The analysis of relaxation times provided in the previous section has indicated that the majority of organic solvents have relaxation times greater than 65 ps (in some cases it is larger than 1000 ps) and therefore it is not surprising that many organic solvents superheat in a microwave cavity. The extent and origins of this phenomenon have been discussed by Baghurst and Mingos.[31] It is not uncommon for organic solvents to exhibit boiling points some 10–20 °C higher than their conventional boiling points in a microwave cavity. These raised boiling points have a number of implications regarding the relative rates of reaction under conventional and microwave conditions. Fig. 10 and Tables 8 and 9 give some data concerning the variations of the dielectric properties of some alcohols as a function of temperature and illustrate the conclusions developed above. Low molecular weight polar organic molecules, *e.g.* MeOH and $CH_3CN$, are rare instances where the relaxation times are very short and where raising the temperature leads to a reduction in loss tangents. For methanol, ethanol and *n*-butanol, the relaxation frequency varies from $<2.45$ GHz at the low temperature end to $>2.45$ GHz at the highest temperature reported (Table 9) therefore thermal runaway effects may diminish as the boiling point is approached.

4. The addition of small amounts of a polar solvent with a large loss tangent usually leads to high heating rates for the whole mixture. The energy transfer between the polar molecules which are coupling with the microwaves and the majority non-polar solvent is rapid and therefore this provides an effective mechanism for introducing non-polar solvents as

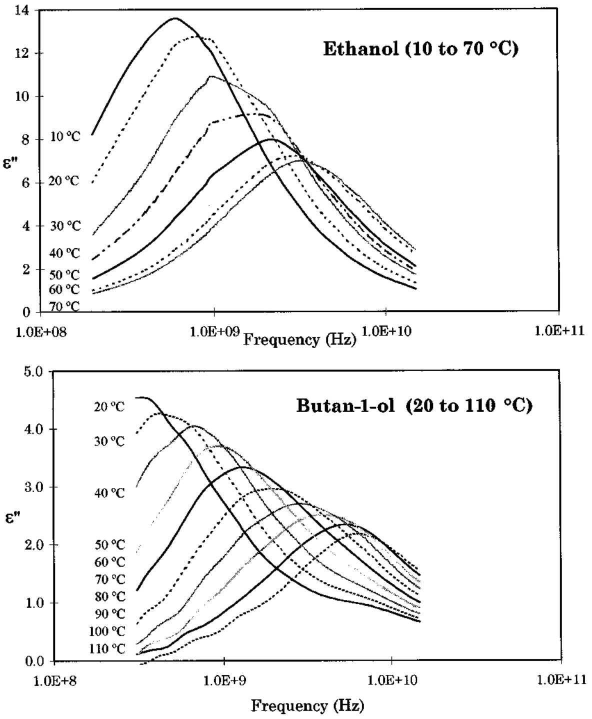


**Fig. 10** Variation of the dielectric properties as a function of temperature

**Table 8** Relaxation times and dielectric properties at 2.45 GHz of propan-1-ol and methanol as a function of temperature

| | | Propanol | | Methanol | | |
|---|---|---|---|---|---|---|
| *T*/°C | *τ*/ps | *ε*′ | *ε*″ | *ε*′ | *ε*″ | *τ*/ps |
| −20 | | 6.33 | 1.34 | 14.75 | 12.59 | 133.6 |
| −10 | | 6.94 | 1.65 | 17.85 | 14.25 | 109.0 |
| 0 | 884 | 6.97 | 2.08 | 20.90 | 16.46 | 96.4 |
| 10 | 548 | 6.87 | 2.59 | 22.63 | 15.32 | 62.6 |
| 20 | 442 | 7.94 | 3.41 | 20.06 | 11.77 | 52.0 |
| 30 | | 17.97 | 11.01 | 24.49 | 12.52 | 40.8 |
| 40 | | | | 24.19 | 10.43 | 34.4 |
| 50 | | | | 23.95 | 8.62 | 28.8 |
| 60 | | | | 19.42 | 6.10 | 26.6 |

coupling agents into a microwave cavity (see Fig. 11 for example).

5. The addition of salts to solvents increases their conductivities and has a dramatic influence on their heating rates.

6. Generally the rate of the rise in temperature of an elemental volume is related to the heat input $\varepsilon''|E|^2$ but the heat is conducted away at a rate which depends upon the thermal diffusivity and the temperature gradient in the sample. An equilibrium temperature is reached when these two terms are equal. Multimode cavities are particularly susceptible to cause thermal runaway in samples which have high loss tangents because of their standing wave characteristics.

7. Table 10 summarises some loss tangent data for some organic solvents as a function of frequency. Clearly for water, methanol and nitrobenzene changing the frequency of the microwave radiation results in a decrease in the loss tangent, but for hexan-1-ol and glycerol which have much longer relaxation times a much larger loss target is observed at 433.9 MHz. Therefore for some solvents with high relaxation times there may be an advantage to using some of the alternative microwave frequencies which have been designated for dielectric heating.

**Table 9** Relaxation times and frequencies and dielectric properties at 2.45 GHz of ethanol and butan-1-ol as a function of temperature

| | Ethanol | | | | Butan-1-ol | | | |
|---|---|---|---|---|---|---|---|---|
| *T*/°C | *fr* GHz | *ε*′ | *ε*″ | *τ*/ps | *fr* GHz | *ε*′ | *ε*″ | *τ*/ps |
| 10 | 0.59 | 7.05 | 5.81 | 269.8 | | 4.22 | 1.16 | |
| 20 | 0.80 | 7.49 | 6.46 | 199.0 | 0.38 | 3.52 | 1.45 | 419.0 |
| 30 | 1.19 | 8.05 | 7.06 | 133.8 | 0.43 | 3.55 | 1.80 | 370.2 |
| 40 | 1.53 | 8.95 | 7.39 | 104.0 | 0.69 | 3.71 | 2.22 | 230.8 |
| 50 | 2.03 | 10.11 | 7.28 | 78.4 | 0.93 | 4.04 | 2.63 | 171.1 |
| 60 | 2.88 | 11.15 | 6.76 | 55.2 | 1.32 | 4.47 | 2.88 | 120.6 |
| 70 | 3.26 | 11.71 | 6.35 | 48.8 | 1.97 | 5.03 | 2.92 | 80.8 |
| 80 | | | | | 2.81 | 5.50 | 2.67 | 56.6 |
| 90 | | | | | 3.90 | 5.75 | 2.28 | 40.8 |
| 100 | | | | | 5.35 | 5.83 | 1.77 | 29.8 |
| 110 | | | | | 6.50 | 5.73 | 1.33 | 24.4 |

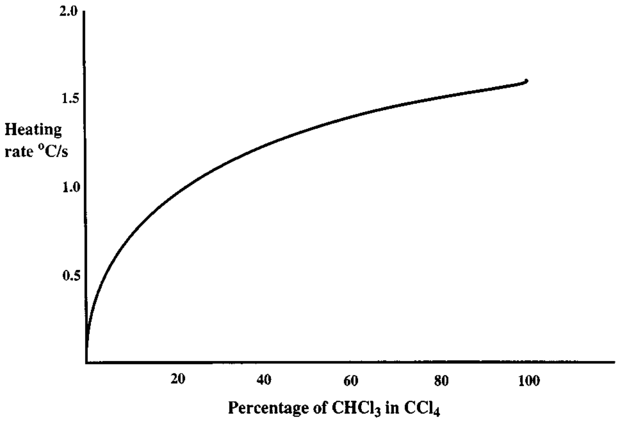


**Fig. 11** Variation in heating rates for a $CHCl_3$–$CCl_4$ mixture

In summary, it may be appreciated that the relaxation times of molecules have a profound influence on the dielectric parameters which influence the rate of heating in a microwave cavity. The relaxation times may involve the whole molecule or a functional group anchored to a large molecule and they depend on the intermolecular forces between the molecules and the size of the molecule. It is hoped the ready access to the data presented in this review will lead to the design of microwave heating experiments which are based more soundly on the relevant dielectric parameters.

## 9 Acknowledgements

BP plc are thanked for endowing D. M. P. Mingos' chair, the EPSRC for financial support and CEM for generously providing equipment.

**Table 10** Loss tangent data for some common solvents as a function of frequency

| | Water | | | Methanol | | | Hexan-1-ol | | | Glycerol | | | Nitrobenzene | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Frequency | e′ | e″ | Tan *δ* | e′ | e″ | Tan *δ* | e′ | e″ | Tan *δ* | e′ | e″ | Tan *δ* | e′ | e″ | Tan *δ* |
| 13.56 MHz | 78.3 | 0.10 | 0.001 | 35.1 | 0.40 | 0.011 | 8.00 | 0.70 | 0.088 | 42.5 | 3.70 | 0.087 | 35.1 | 0.20 | 0.006 |
| 27.12 MHz | 78.4 | 0.10 | 0.001 | 35.0 | 0.50 | 0.014 | 9.30 | 0.90 | 0.097 | 42.1 | 8.30 | 0.197 | 35.2 | 0.40 | 0.011 |
| 433.9 MHz | 78.5 | 1.70 | 0.022 | 34.2 | 4.44 | 0.130 | 5.16 | 3.62 | 0.702 | 11.4 | 9.87 | 0.866 | 35.3 | 3.98 | 0.113 |
| 900 MHz | 78.6 | 3.51 | 0.045 | 32.1 | 8.49 | 0.265 | 3.96 | 2.25 | 0.568 | 8.41 | 6.39 | 0.759 | 33.7 | 7.73 | 0.229 |
| 2.45 GHz | 77.4 | 9.48 | 0.122 | 21.9 | 14.6 | 0.665 | 3.43 | 1.17 | 0.341 | 6.33 | 3.42 | 0.540 | 25.2 | 14.7 | 0.584 |

## 10 References

1 R. Dayani, Molecular Magic with Microwaves, *Chem. Eng. News*, 1997, Feb 10th, 26.

2 A. R. von Hippel, *Dielectric Materials and Applications*, MIT Press, Cambridge, Mass., USA, 1954.

3 A. R. von Hippel, *Dielectric and Waves*, MIT Press, Massachusetts Institute of Technology, Cambridge, Mass USA, 1954.

4 C. Gabriel, S. Gabriel and E. Courtout, *Phys. Med. Biol.*, 1996, **41**, 2231.

5 E. H. Grant, R. J. Sheppard and G. P. South, *Dielectric Behaviour of Biological Molecules in Solution*, Clarendon Press, Oxford, UK, 1978.

6 E. H. Grant, *IEE Proc. ptA*, 1981, **128**, 602.

7 D. Q. M. Craig, *Dielectric Analysis of Pharmaceucitical Systems*, Taylor and Francis, London, UK, 1995.

8 H. M. Kingston and S. J. Haswell, *Microwave Enhanced Chemistry*, American Chemical Society, Washington DC, USA, 1997.

9 R. Lauvert, A. Laporterie, J. Dubac, J. Berlan, S. Lefeuvre and M. Auchay, *J. Org. Chem.*, 1992, **57**, 7099 and references therein.

10 R. D. Raner, C. R. Strauss, F. Vyskoc and L. Mokbel, *J. Org. Chem.*, 1993, **58**, 950.

11 S. A. Galema, *Chem. Soc. Rev.*, 1997, **26**, 233.

12 D. M. P. Mingos and A. G. Whittaker, *J. Chem. Soc. Dalton Trans.*, 1992, 2751.

13 D. R. Baghurst and D. M. P. Mingos, *Chem. Soc. Rev.*, 1991, **20**, 1.

14 G. Majetich and K. Wheless, ref. 8, p 455; D. R. Baghurst and D. M. P. Mingos, ref. 8, p. 523.

15 The data given in the Tables represent a combination of literature data (see particularly references 7, 16 and 17 for general compilations and the Tables for specific references) and recent redeterminations in our laboratories using the methods described in C. Gabriel, T. Y. A. Chan and E. H. Grant, *Phys. Med. Biol.*, 1994, **34**, 2183.

16 N. E. Hill, W. E. Vaughan, A. H. Price and M. Davies, *Dielectric Properties and Molecular Behaviour*, van Nostrand, New York, 1969.

17 M. Davies, *Some Electrical and Optical Aspects of Molecular Behaviour*, Commonwealth and International Library of Science, Technology and Liberal Studies, Pergamon Press, Oxford, 1962.

18 H. J. Liebe, G. A. Hufford and T. Manabe, *Int. J. Infrared Millimetre Waves*, 1991, **12**, 659.

19 A. Stogryn, *IEEE Transaction on microwave theory and techniques*, 1971, **19**, 733.

20 J. B. Bateman and C. Gabriel, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 355.

21 D. W. Davidson and R. H. Cole, *J. Chem. Phys.*, 1951, **19**, 1484; K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 1941, **9**, 341.

22 S. E. Keefe and E. H. Grant, *Phys. Med. Biol.*, 1974, **19**, 201.

23 E. H. Grant, *J. Mol. Biol.*, 1966, **19**, 133.

24 E. H. Grant, G. P. South, S. Takashima and H. Ichimura, *Biochem. J.*, 1971, **122**, 691.

25 E. H. Grant, R. J. Sheppard, G. L. Mills and J. Slack, *Lancet*, 1972, 159.

26 J. B. Hasted, *Aqueous Dielectrics*, Chapman and Hall, London, UK, 1973.

27 B. P. Jordan, R. J. Sheppard and E. H. Grant, *J. Appl. Phys.*, 1972, **11**, 675.

28 J. G. Kirkwood, *J. Chem. Phys.*, 1939, **7**, 911.

29 A. C. Metaxas and R. J. Meredith, *Industrial Microwave Heating*, Peter Peregrinces, Institution of Electrical Engineers, Exeter, 1982.

30 D. R. Baghurst and D. M. P. Mingos, *J. Chem. Soc. Chem. Commun.*, 1992, 674.

31 D. C. Dibben and A. C. Metaxas *J. Microwave Power*, 1994, **29**, 242.

*Received 26th January 1998*
*Accepted 12th February 1998*