DEDUCING THE RELAXATION TIMES OF SOME POLAR SOLVENTS USING COLE-COLE RELAXATION MODEL.

[1]Musa, N., [2]Onimisi, M. Y. and [3]Ikyumbur, J. T.
[1]Department of Applied Physics, Kaduna Polytechnic, Kaduna.
[2] Department of Physics, Nigerian Defence Academy, Kaduna.
[3] Department of Physics, Benue State University, Makurdi.
Correspondence: nmusa@kadunapolytechnic.edu.ng +2348034518574.

ABSTRACT

A study of the relaxation times of some polar solvents was carried out using the Cole-Cole relaxation model. The solvents; Methanol, Ethanol, Butan-1-ol were studied. The study was carried out within a frequency range of 100kHz and 50MHz and a temperature range of 10^0C and 50^0C. The following relaxation times: 0.09273 ns, 0.04073 ns, 0.03138 ns, 0.02082 ns and 0.01439 ns for methanol; 0.9360 ns, 0.6132 ns, 0.4031 ns, 0.2713 ns and 0.1812 ns for ethanol and 0.2385 ns, 0.1931 ns, 0.1424 ns, 0.1059 ns and 0.0796 ns for butan-1-ol at 10^OC, 20^OC, 30^OC, 40^OC and 50^OC respectively were deduced using the slopes of the graphs plotted from the derived equation. The linear fit of the plotted points converged at the origin. The R^2 values for each solvent under investigation, fitted perfectly. This eliminates the need for elaborate experimental analysis. As the temperature increases, the relaxation time decreased. These results can be used in drug design and synthesis at radio wave frequency range.

Keywords: Relaxation Times, Polar Solvents, Cole-Cole Model.

INTRODUCTION

Solvents that are polar protic and polar aprotic are frequently employed in manufacturing sectors. The understanding of dielectric characteristics is used by the food, medicinal, chemical, and pharmaceutical sectors at every stage of manufacturing. Poorly soluble medications, for instance, are a challenge in pharmaceutical formulation, thus the pharmaceutical industry continuously uses water and organic solvents in their manufacturing (Craig, 1995; Behera et al. 2010). Since drug solubility is a key consideration in the discovery and formulation of new medications, improving dissolving characteristics is a significant challenge. Most pharmaceutical materials are thermally sensitive such that drying them under reduced temperature or in vacuum is necessary. This necessitates a long drying time. Radio and microwaves offer an alternative and faster method for the removal of moisture (Satyendra, 2018). Any liquid that helps a solute dissolve is a solvent. The element that is more abundant in a solution is the solvent. In daily life, water is presumably the most prevalent solvent. Organic substances like benzene, tetrachloroethylene, or turpentine make up a large portion of other solvents (Crossley, 2012). A general rule in chemistry is that non-polar solvents, like gasoline, dissolve non-polar compounds like wax, whereas solvents made up of polar molecules, like water, dissolve other polar molecules, like table salt. The solubility of a given solute refers to how easily it dissolves in a given solvent. For instance, ethanol is very water soluble. Oil and vinegar don't mix well and will quickly separate into two layers even after a vigorous shake (Das Gupta *et al.*, 1999).

CHARACTERISTICS OF POLAR PROTIC AND NON PROTIC SOLVENTS

The **key difference** between protic and aprotic solvents is that **protic solvents have dissociable hydrogen atoms whereas aprotic solvents have no dissociable hydrogen atom**.

A solvent is a liquid compound that can dissolve other substances. There are different forms of solvents that can be categorized basically into two group as polar and non-polar solvents. The polar solvents can be divided into two groups as protic and aprotic solvents. Protic solvents can form hydrogen bond because they have chemical bonds required for the hydrogen bonding, i.e. O-H bond and N-H bond. In contrast, aprotic solvents lack those chemical bonds required for hydrogen bonding (Ikyumbur, 2019).

Dielectric Polarization and Dielectric Relaxations

Free charges in a conductor will respond to exactly cancel an applied field. The charges in an insulator will respond to an applied field in such a way as to partially cancel an applied electric field (Frohlich, 2018). In dielectrics, the rates with which polarization can occur are limited, so that as the frequency of the applied electric field is increased some polarization will no longer be able to attain their low frequency or d.c values. The dipole moments are just not able to orient fast enough to keep in alignment with the applied field and the total polarizability falls from α_T to $(\alpha_T - \alpha_0)$. This fall, with its related reduction of permittivity, and the occurrence of energy absorption, is referred to as dielectric relaxation or dispersions (Agilent, 2006).

RELAXATION MODELS

There are many relaxation models as there are solvents and crystals. The most recognized relaxation models include the Debye model (Progenitor), Cole-Cole model, Havrilak-Negami model etc. The Debye model is deficient in studying relaxation times under the radio-frequency range. The best model to study solvents under that frequency range is the Cole-Cole relaxation model. Polar dielectrics that have more than one relaxation time satisfy the Cole-Cole equation. The plot ε″ versus ε′ will be distorted, and Cole–Cole relaxation showed that the plot will still be a semicircle with its center displaced below the ε′ axis. They suggested an empirical equation for the complex dielectric constant as (Cole and Cole, 1941)

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

Equation (1) can be separated into its real and imaginary parts thus

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)\left(1 + (\omega\tau)^{1-\alpha} Sin\ \alpha\frac{\pi}{2}\right)}{1 + 2(\omega\tau)^{1-\alpha}\ Sin\ \alpha\frac{\pi}{2} + (\omega\tau)^{2(1-\alpha)}} \tag{2}$$

$$\varepsilon'' = \frac{\left((\varepsilon_s - \varepsilon_\infty)(\omega\tau)^{1-\alpha}\ Cos\alpha\frac{\pi}{2}\right)}{1 + 2\ (\omega\tau)^{1-\alpha} Sin\ \alpha\frac{\pi}{2} + (\omega\tau)^{2(1-\alpha)}} \tag{3}$$

And

Where ε’ is the dielectric constant and ε’’ is the loss factor, ω is the angular frequency, τ is the relation time, ε_0 and ε_∞ are the zero and infinite values of the dielectric constant and α is the distribution factor.

THE COLE-COLE CURVE EQUATION

The Cole-Cole plots have been used widely to analyze the results obtained for the dielectric measurements in many polar liquids. The Cole-Cole Curve equation is given by (Cole and Cole, 1941)

$$\therefore \quad \left(\varepsilon' - \frac{(\varepsilon_S + \varepsilon_\infty)}{2}\right)^2 + \left(\varepsilon'' + \frac{\tan\delta}{2}(\varepsilon_S - \varepsilon_\infty)\right)^2 = \left(\frac{(\varepsilon_S - \varepsilon_\infty)}{2}\right)^2 (sec^2\,\delta) \tag{4}$$

where δ = π/2 is the tangential angle subtended by the centre of the circle defined by equation(4)

This is an equation of a circle with centre at $\left(\frac{(\varepsilon_S+\varepsilon_\infty)}{2}, -\frac{(\varepsilon_s-\varepsilon_\infty)}{2}\tan\left(\frac{\alpha\pi}{2}\right)\right)$ and having a radius $\frac{(\varepsilon_S-\varepsilon_\infty)}{2}\sec\left(\frac{\alpha\pi}{2}\right)$

It can be seen that the y coordinate of the center is negative. This implies that the center lies below the ε' axis.

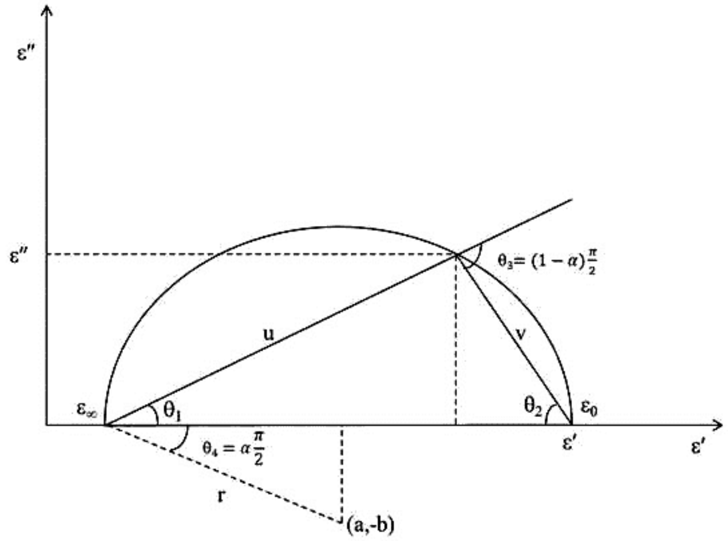

Figure 1: Argand plot of the Cole-Cole equation (Musa et al., 2020).

COLE-COLE RELAXATION TIME AND RELAXATION FREQUENCY

This is an attempt to derive an equation that can be used to obtain the relaxation times and by extension, the relaxation frequencies of the solvents of interest.

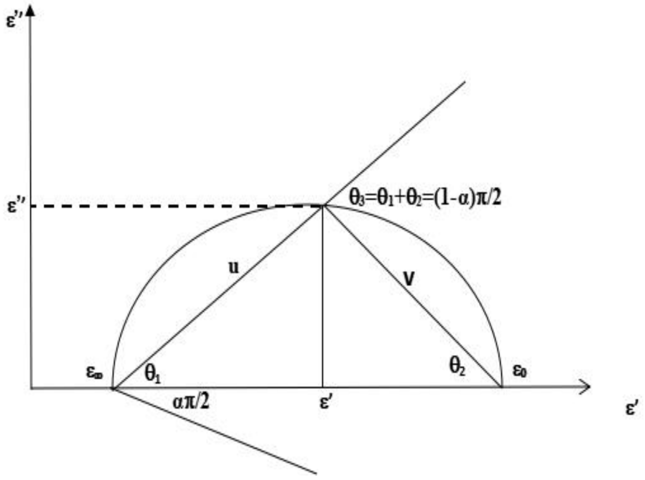

Figure 2: Cole-Cole argand plot showing points of interest (Musa et al., 2020)

From Equation (1) $\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0-\varepsilon_\infty}{1+(i\omega\tau)^{1-\alpha}}$

Also, $\varepsilon^* = \varepsilon' - i\varepsilon''$

From Fig 2, it can be seen that

$$u^2 = (\varepsilon' - \varepsilon_0)^2 + \varepsilon''^2 \qquad (5)$$

$$v^2 = (\varepsilon_\infty - \varepsilon')^2 + \varepsilon''^2 \qquad (6)$$

This implies that equations (5) and (6) can be written as

$$\left|\frac{v}{u}\right| = \frac{(\varepsilon_\infty - \varepsilon\prime)^2 + \varepsilon\prime\prime^2}{(\varepsilon\prime - \varepsilon_0)^2 + \varepsilon\prime\prime^2} \qquad (7)$$

From (Day and Underwood 2013) it can be seen from Fig. 2 that

$$u = \varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \qquad (8)$$

And

$$v = \varepsilon_0 - \varepsilon^* = \varepsilon_0 - \left(\varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}\right) \qquad (9)$$

$$\Rightarrow\ v = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}(i\omega\tau)^{1-\alpha} = u(i\omega\tau)^{1-\alpha} \qquad (10)$$

$$\therefore\ \frac{v}{u} = (i\omega\tau)^{1-\alpha} \qquad (11)$$

$$\text{And } \left|\frac{v}{u}\right| = (\omega\tau)^{2(1-\alpha)} \qquad (12)$$

$$\Rightarrow\quad (\omega\tau)^{2(1-\alpha)} = \frac{(\varepsilon_\infty - \varepsilon\prime)^2 + \varepsilon\prime\prime^2}{(\varepsilon\prime - \varepsilon_0)^2 + \varepsilon\prime\prime^2} \qquad (13)$$

And

$$\omega\tau = \left[\frac{(\varepsilon_\infty - \varepsilon\prime)^2 + \varepsilon\prime\prime^2}{(\varepsilon\prime - \varepsilon_0)^2 + \varepsilon\prime\prime^2}\right]^{\frac{1}{2(1-\alpha)}} \qquad (14)$$

If the RHS of equation(14) is the vertical (y) axis, then a graph of y against ω will produce a straight line graph from the origin,with a slope τ_m which represents the mean relaxation time. Obtaining the relaxation time leads to deducing the relaxation frequency, f_m.

METHODOLOGY

CHOICE OF SOLVENTS

The solvents were chosen due to their wide range of use in pharmaceutical, food, paint and other chemical industries. The static and complex dielectric constants of the solvents used, was adapted from the database of solvents: The National Physical Laboratory (MAT-23) (Gregory and Clarke, 2012). It formed the basis for comparison with the Cole-Cole relaxation data generated from this work.

Table 1: Static and complex permittivities and relaxation times of Methanol (Gregory and Clarke, 2012)

Temperature (^{0}C)	ε_s	ε_∞
10	35.74	5.818
20	33.64	5.654
30	31.69	5.450
40	29.85	5.251
50	28.19	5.224

Table 2: The static and complex permittivities and relaxation times of Butan-1-ol (Gregory and Clarke, 2012)

Temperature (^{0}C)	ε_s	ε_∞
10	19.54	3.412

20	18.19	3.406
30	16.89	3.418
40	15.65	3.418
50	14.44	3.416

Table 3: Static and complex permittivities and relaxation times of Ethanol (Gregory and Clarke, 2012)

Temperature (^{0}C)	ε_s	ε_∞
10	26.79	4.62
20	33.64	4.53
30	31.69	4.47
40	29.85	4.10
50	28.19	4.38

FLOWCHART FOR COLE-COLE RELAXATION MODEL

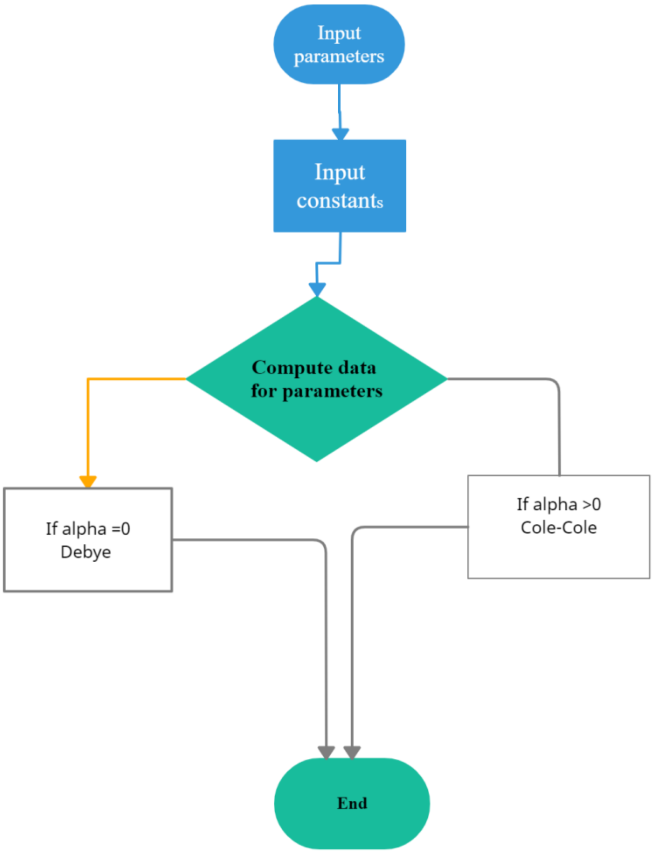

Figure 3: Flowchart showing the steps in computing the dielectric parameters

ALGORITHM FOR CALCULATING THE DIELECTRIC AND LOSS FACTORS

The algorithms used in calculating the values of the dielectric and loss factors for the Debye and Cole-Cole relaxation equations were designed using MAPLE 17 programming language. For the Cole-Cole relaxation formula, $\alpha = 0.5$ was adapted to observe the broadness of the curve. Replacing $\alpha = 0.5$ with $\alpha = 0$ converts the Cole-Cole relaxation equation to that of

Debye. The temperature range is from 10^0C to 50^0C and frequency range from 100kHz to 50MHz. This covers the radio frequency range up to the microwave range.

From the flowchart in fig. 3, the local variables to be calculated (ε', ε'', δ) and constants (τ, π, ω, α, ε_0, ε_∞) were defined.

The local variables will then be used to calculate the values of the parameters of interest.

If $\alpha = 0$, the values obtained are the Debye relaxation model parameters. If $\alpha > 0$, that is the Cole-Cole relaxation model parameters.

#Maple Programme to calculate ε_0, ε_∞ and tan δ for methanol at 10^0C

```
local $ES, EZ, E1, E11, \omega, \pi, \tau, \alpha, tan\delta$;   #Defining the local variables to be used
$E_S := 19.54$: # The Static permittivity $\varepsilon_0$
$E_Z := 3.412$: # The complex permittivity $\varepsilon_\infty$
$\pi := 3.142$: # The value of $\pi$
$\tau := 9.306.10 \cdot\cdot (-10)$: # Relaxation time in seconds
$\omega := 2000.\pi.f$: # Angular frequency, 1000 was multiplied to $2\pi f$ for simplicity
$\alpha_{CC} := 0.5$: # The Cole
                    – Cole distribution factor: this defines the shape of the argand plot
$\alpha_D := 0$: # The Debye distribution factor: this defines the shape of the Cole
                    – Cole plot
for f from 100 by 100 to 50000 do
$E_Z + \frac{(E_S - E_Z).\left(1 + (\omega \cdot \tau)^{(1-\alpha)} \cdot sin\left(\frac{\alpha \cdot \pi}{2}\right)\right)}{\left(1 + 2(\omega \cdot \tau)^{(1-\alpha)} \cdot sin\left(\frac{\alpha \cdot \pi}{2}\right) + (\omega \cdot \tau)^{2 \cdot (1-\alpha)}\right)}$,
            #Formula for calculating Dielectric constant, $\varepsilon'$
$\frac{(E_S - E_Z).\left((\omega \cdot \tau)^{(1-\alpha)} \cdot cos\left(\frac{\alpha \cdot \pi}{2}\right)\right)}{\left(1 + 2(\omega \cdot \tau)^{(1-\alpha)} \cdot sin\left(\frac{\alpha \cdot \pi}{2}\right) + (\omega \cdot \tau)^{2 \cdot (1-\alpha)}\right)}$, #Formula for calculating Loss Factor, $\varepsilon''$
end do
Print (f, E1, E11) # this will print the frequency, dielectric constant and loss factor
```

The result obtained is in the *.txt* format. It is then opened as a *.csv* file on Microsoft Excel. Then transferred to Originlab software for graphing and interpretation.

RESULTS AND DISCUSSION

Deducing Mean Relaxation Time (τ_m)

Based on the derivation of equation 12, a graph of y against was plotted. From the equation, it can be seen that a linear graph will be obtained with intercept on the origin. The slopes of the temperature dependent linear graphs will be the respective relaxation times for the temperatures.

Figures 4, 5 and 6 show the straight line graphs for the solvents of interest. Tables 4, 5 and 6 show the temperatures and corresponding relaxation times in nanoseconds.

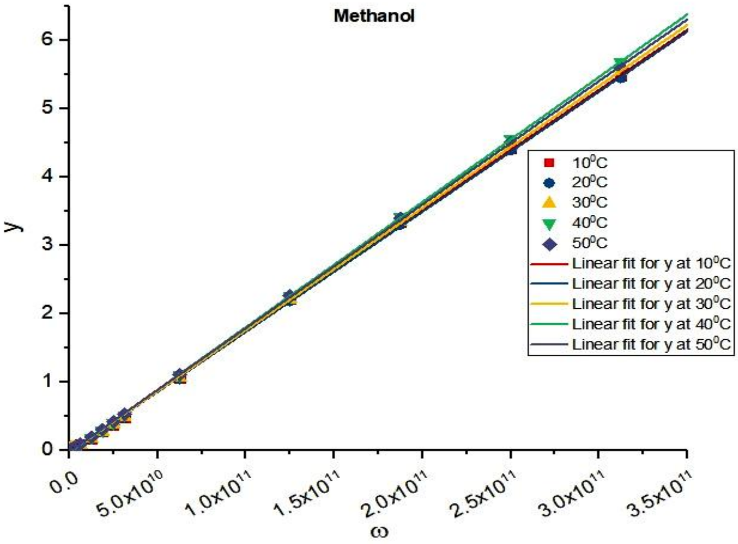

Figure 4: Graph of y against w to deduce t for methanol

Table 4: Deduced values of τ for the temperature range (10^0C to 50^0C) for methanol

Temperature (^{0}C)	Relaxation time (τ_m) (ns)	R^2 value for fitted line
10	0.09273	1
20	0.04073	1
30	0.03138	1
40	0.02082	1
50	0.01439	1

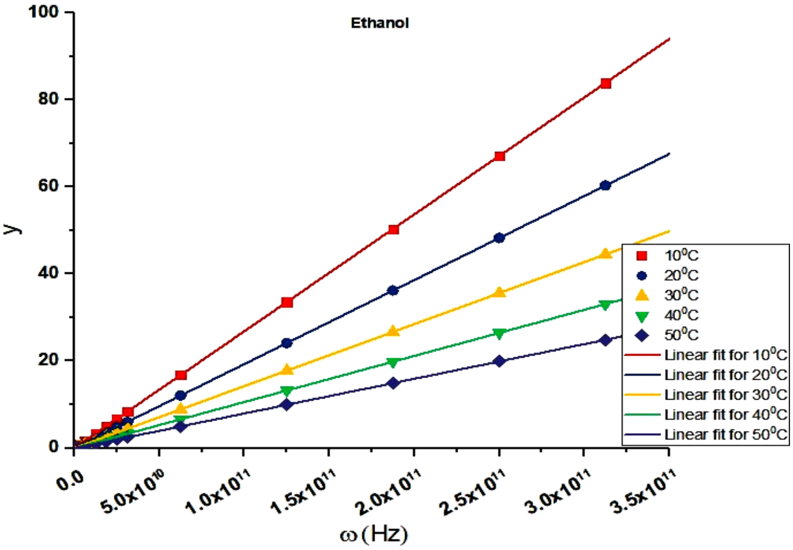

Figure 5: Graph of y against w to deduce t for ethanol

Table 5: Deduced values of τ for the temperature range (10^{0}C to 50^{0}C) for ethanol

Temperature (^{0}C)	Relaxation time (τ_m) (ns)	R^2 value for fitted line
10	0.9360	1
20	0.6132	1
30	0.4031	1
40	0.2713	1
50	0.1812	1

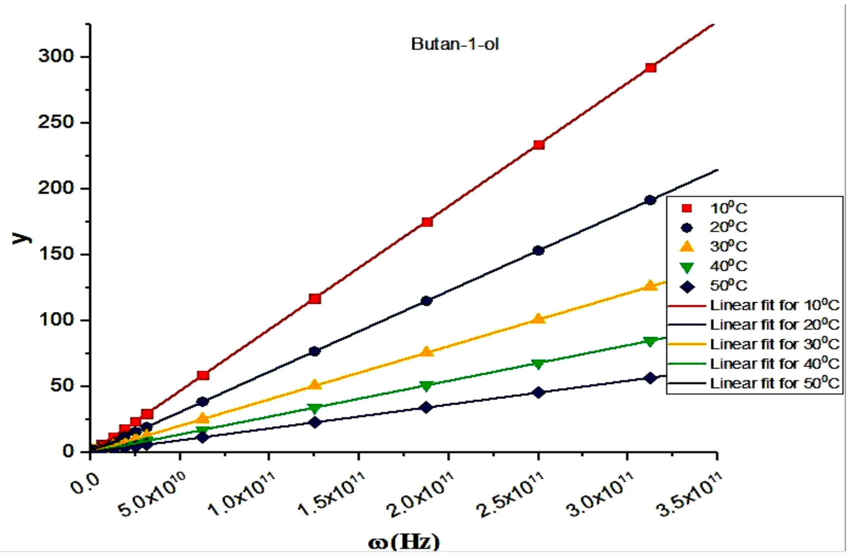

Figure 6: Graph of y against w to deduce t for butan-1-ol

Table 6: Deduced values of τ for the temperature range (10^{0}C to 50^{0}C) butan-1-ol

Temperature (^{0}C)	Relaxation time (τ_m) (ns)	R^2 value for fitted line
10	0.2385	1
20	0.1931	1
30	0.1424	1
40	0.1059	1
50	0.0796	1

For all the solvents of interest, there is a fall in the relaxation time as the temperature increased. For methanol, the relaxation time was 0.09273 ns at 10^{0}C and 0.01439 ns at 50^{0}C. This pattern was also observed for ethanol (0.9360 at 10^{0}C and 0.1812 at 50^{0}C) and butan-1-ol (0.2385 at10^{0}C and 0.0796 at 50^{0}C) as shown in tables 5 and 6 respectively. These changes can be attributed to the slow response of the molecules of the solvents in keeping up with the periodic fluctuation of the electric field and its own disorientation due to the rise in temperature. The interplay of forces, causes the relaxation time to fall as the temperature rises. The increase in the inter-atomic distance between the molecules due to the rise in temperature could also be linked to the fall in relaxation time as the temperature increased. The R^2 values for the fitted lines for all solvents at the temperatures of interest showed that the lines were well fitted. The relaxation time leads us to calculate the relaxation frequencies for the solvents of interest.

CONCLUSION

The relaxation times for methanol, ethanol and butan-1-ol between 10^0C - 50^0C was successfully deduced from the slopes of the linear fits of the graphs. The R^2 values showed perfect fit. The results obtained for all the solvents, showed that as the temperature increases, the relaxation time reduces. This could be attributed to interaction between the fluctuating electric field and temperature change taking place. Another reason could be the increase in the inter-atomic distance between the molecules

The results obtained can be used to design and synthesize drugs within the radiowave frequency range using the Cole-Cole relaxation model.

REFERENCES

Agilent (2006). Basics of Measuring the Dielectric Properties. http://www3.imperial.ac.uk/pls/portallive/docs/1/11949698.PDF

Behera, A.L., Sahoo, S.K., and Patil, S.V. (2010). Enhancement of Solubility; A pharmaceutical Overview. *Der. Pharmacia Lett*. 2(2): 310-318.

Craig, DQ. M. (1995). Dielectric Analysis of Pharmaceutical Systems, Taylor & Francis. London.

Crossley, J. (2012). Dielectric relaxation and hydrogen bonding in liquids. *Advances in molecular relaxation processes*, 2(1): 69-99.

Das Gupta , D. K. and Scarpa, P. C. N. (1999).“Modeling of Dielectric Relaxation Spectra of Polymers in the Condensed Phase,”IEEE Electr. Insul. Mag., Vol. 15, 23–32,

Day, K and Underwood, P (2013). Dielectric relaxation in solvents. *Advances in molecular relaxation processes,* 2(2): 72-90

Frohlich, H., (2018). Theory of dielectrics, Oxford University Press, Oxford.

Gregory, A.P. and Clarke, R.N. (2012). Tables of complex permittivity of dielectric reference liquids at frequencies up to 5 GHz. NPL Report MAT 23.

Ikyumbur, T.J.(2019). Analysis of the behaviour of the dielectric properties of ethanol used by pharmaceutical industries in Cole-Cole and Debye relaxation models.A paper presented at the Nigerian Institute of Physics conference 2019 Owerri, Nigeria.

Musa, N, Onimisi, M.Y and Ikyumbur, J.T. (2020). Frequency and temperature dependence of ethanol using the Cole-Cole relaxation model. *American Journal of Condensed Matter Physics* 10(2): 44-49. DOI: 10.5923/j.ajcmp.2020100203.03

Satyendra, P.S. (2018). An Analysis of Dielectric parameters and penetration depth of tomato sauces. *J. Food Process Technol* 9(7) ISSN: 2157-7110.