Evidence for the existence of multiple equilibrium states in cobalt phthalocyanine tetramer: a study by dielectric spectroscopy

Evidence for the existence of multiple equilibrium states in cobalt phthalocyanine tetramer: a study by dielectric spectroscopy

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Abstract
In any investigation, information about the molecules under consideration is very essential for tailoring their properties. Evaluation of dispersion parameters, namely optical dielectric constant, static dielectric constant, relaxation time and spreading factor, assumes significance in this context. Dielectric spectroscopy is a useful tool for estimating these parameters. Not only does it reveal details about these constants but it also gives insight into the mechanism of conduction. In this paper the evaluation of dispersion parameters of cobalt phthalocyanine tetramer in the temperature range 300–393 K is attempted using Cole–Cole plots. The temperature variation of the spreading factor indicates the existence of multiple equilibrium positions in the case of cobalt phthalocyanine tetramer. To the best of our knowledge, the evaluation of dispersion parameters for cobalt phthalocyanine tetramer is reported for the first time.

1. Introduction

Polymers and polymer-based materials have received wider attention during the last two decades or so because of the possibility of realizing very many devices based on polymers. The emergence of new disciplines like organic semiconductors and molecular electronics has augmented the ongoing research activities in this area. Among polymers, metallo and metal-free phthalocyanines are in the forefront because of their unique photoconductivity and semiconducting properties [1–7]. Phthalocyanines are increasingly being employed in various devices such as solar cells, electrophotography, gas sensors, rectifying devices, electrochromism, LB films and liquid crystals [8, 9]. They are employed as the active component in organic solar cells, since they undergo

structural self-organization which is reflected in an effective electromagnetic migration in the form of exciton transport [10]. Phthalocyanine and their derivatives are also extensively employed as photoconductivity material in laser printers and light absorbing layers in recordable CDs, photo sensitizers in laser cancer therapy, non-linear optical material and industrial catalysts. The annular structures of phthalocyanine give solidity by forming a strong and extremely stable chemical bond. The electrical properties of polymeric phthalocyanines are of interest because of their excellent stability against light, heat, moisture and air. Hence polymeric phthalocyanines are suitable candidates for use as environmentally stable, electrically conductive materials [11–14]. The extended conjugated structure contributes to the high conductivity of the polymeric metallo phthalocyanines of cobalt, copper and nickel. Among them, cobalt phthalocyanine tetramer exhibits higher electrical conductivity [14–16].

Thus cobalt phthalocyanine, among other phthalocyanines, occupies an important role and extensive studies on the

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structural and electrical properties are underway [17]. A survey of the literature reveals that studies relating to evaluation of dispersion parameters of cobalt phthalocyanine tetramer do not exist and hence evaluation of these parameters assumes significance. In any investigation involving polymers, an insight into the molecule is obtained by the evaluation of parameters like optical dielectric constant, static dielectric constant, average relaxation time, molecular relaxation time and spreading factor. These parameters have a direct bearing on the optical and electrical properties of the polymer. The structure property relationship leads to tailoring of the polymers for applications. Evaluation of dispersion parameters are not straightforward and often involve indirect methods. One such method is to evaluate these parameters with the help of dielectric spectroscopy. Considerable progress has been made since the early days of Cole and Cole [18] in utilizing dielectric spectroscopy to explain the dielectric behaviour and electrical conductivity of a wide range of solid state materials [19]. Dielectric spectroscopy has been found to be a valuable tool in understanding the phenomenon of charge transport in conducting polymers [20]. This investigation has been carried out primarily with the following objectives in mind.

(a) To synthesize cobalt phthalocyanine tetramer and to evaluate its optical dielectric constant, static dielectric constant, relaxation time and spreading factor in the temperature range 300–393 K using dielectric spectroscopy as a tool.

(b) To study the variation of spreading factor with temperature. This will possibly shed light on the mechanism of conduction with respect to the available electronic states in the molecule [21].

It has been generally perceived that molecules having similar structure are believed to have only two equilibrium states [22]. However, the presence of multiple states in a molecule can be inferred by evaluating the spreading factor at different temperatures. In this study permittivity and loss factor are evaluated using an LCR meter. Cole–Cole plots are drawn and, based on a simple code used in conjunction with a virtual instrumentation package called LabVIEW, we were able to automate the evaluation of optical dielectric constant, static dielectric constant, relaxation time and spreading factor with temperature. Though the literature is replete with valuable information on the dielectric properties of tetrameric cobalt phthalocyanine [12,17,23], it is to be noted here that to the best of our knowledge the evaluation of optical dielectric constant, static dielectric constant, relaxation time and spreading factor on cobalt phthalocyanine tetramer in the temperature range 300–393 K is reported for the first time.

2. Sample preparation and experiment

Tetrameric cobalt phthalocyanine was prepared, purified and characterized by the method reported elsewhere [24, 25]. In brief, in this method cobalt sulfate, pyromellitic dianhydride, excess urea, ammonium chloride and ammonium molybdate were ground well and heated at $180\,^\circ\text{C}$ in nitrobenzene media for 12 h. The reaction mixture was then cooled and washed with methanol several times to remove nitrobenzene. The product was further boiled with $2N$ sodium hydroxide
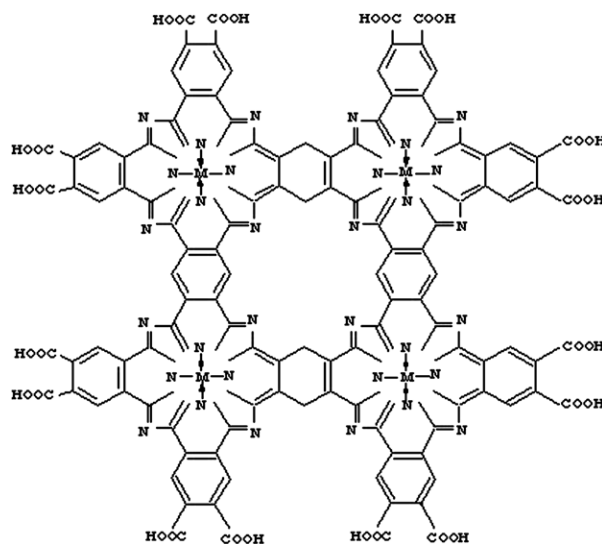
Figure 1. Molecular structure of cobalt phthalocyanine tetramer.

containing sodium chloride and filtered. The filtrate was acidified with hydrochloric acid and washed several times and then dried to obtain phthalocyanine tetramer. Elemental analysis of cobalt phthalocyanine tetramer has been carried out and reported elsewhere [17]. The molecular structure of cobalt phthalocyanine tetramer is shown in figure 1.

The dielectric permittivity measurements on cobalt phthalocyanine tetramer were carried out using a home-made dielectric cell and an HP 4285 LCR meter in the frequency range 100 KHz–10 MHz from 300 to 393 K. The principle of parallel plate capacitor was employed for the evaluation of permittivity. The LCR meter was interfaced with a PC using a virtual instrumentation package called LabVIEW. With this provision around 20 000 data points could be acquired in a matter of 4–5 min. The real value of permittivity is determined from the capacitance value and the imaginary part of permittivity is then evaluated from the loss factor. Further, the Cole–Cole plots for different temperatures are drawn by using circle least square method [26] utilizing the real and imaginary values of dielectric permittivity. Dispersion parameters were evaluated from Cole–Cole plots in the temperature range 300–393 K. A very brief outline of the theory involved in the evaluation of dispersion parameters is provided in the ensuing section.

3. Theory

The Debye relaxation model has been widely employed in describing the response of molecules to an applied electric field. It is based on the assumption that the polarization reaches an equilibrium state exponentially and the superposition principle is applicable in the relaxation phenomena [27]. By Debye theory, the variation of permittivity with frequency is due to the opposition of orientation of polar molecules in an alternating current field by the effects of thermal agitation and molecular interactions. The Debye equation can be written in the form

$$\varepsilon^* - \varepsilon_\infty = \frac{(\varepsilon_s - \varepsilon_\infty)}{(1 + j\omega\tau)}, \tag{1}$$
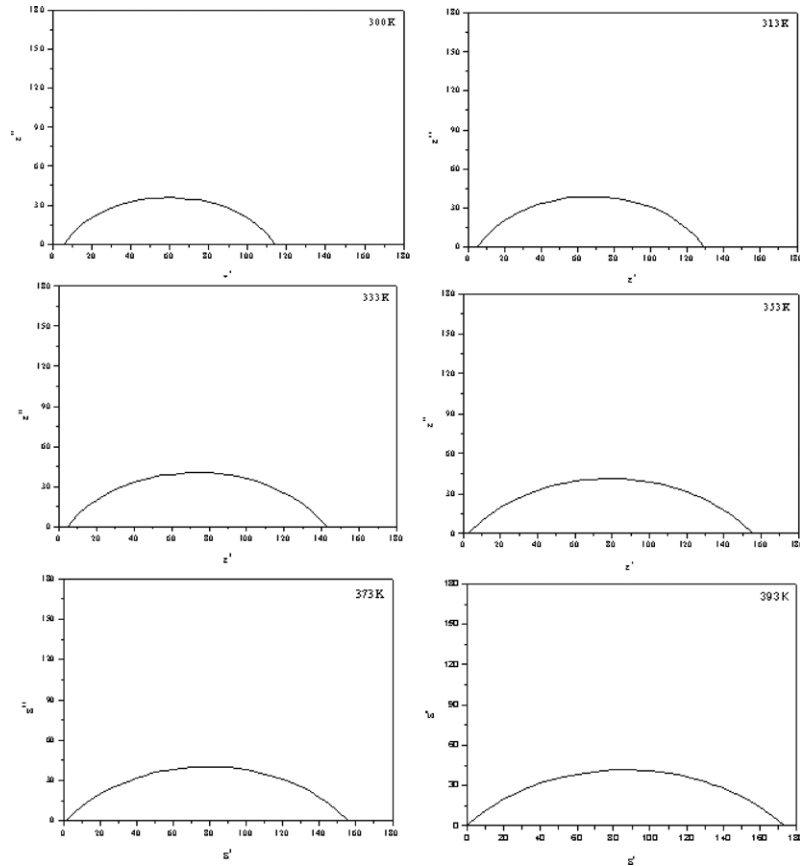
Figure 2. Cole–Cole plots for cobalt phthalocyanine tetramer at different temperatures.

where ε^* is the complex permittivity, ε_∞ is the optical dielectric constant, ε_s is the static dielectric constant, $\omega = 2\pi f$ and τ is the relaxation time. The Cole–Cole plots in such cases are semicircular with the centre on the real axis. However, materials possessing long chain molecules and polymers exhibit broader dispersion and reduced maximum loss than would be expected from molecules obeying ideal Debye behaviour [22]. K S Cole and R H Cole suggested that in this case the permittivity might follow the empirical relation of the form

$$\varepsilon^* - \varepsilon_\infty = \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + (j\omega\tau_0)^{1-\alpha}}, \tag{2}$$

where τ_0 is the average relaxation time and α is the spreading factor of actual relaxation time τ about its mean value τ_0, where α lies in the range 0 to 1.

When $\alpha = 0$, the above equation reduces to Debye's equation. Under such circumstances the Cole–Cole plot is a circular arc with its centre lying below the real axis. The spreading factor α can be deduced from the expression for the maximum value of the imaginary part of permittivity:

$$\varepsilon''_{\max} = \frac{(\varepsilon_s - \varepsilon_\infty)\tan[(1-\alpha)\pi/4]}{2}. \tag{3}$$

The average relaxation time τ_0 can be calculated from the expression

$$\frac{(\varepsilon_0 - \varepsilon')^2 + \varepsilon''^2}{(\varepsilon' - \varepsilon_\infty)^2 + \varepsilon''^2} = (j\omega\tau_0)^{2(1-\alpha)}. \tag{4}$$

The molecular relaxation time can be estimated by employing the following equation by substituting the value of τ_0:

$$\tau = [(2\varepsilon_s + \varepsilon_\infty)/3\varepsilon_s]\tau_0. \tag{5}$$

A detailed description of these derivations is provided elsewhere [18, 22, 32].

4. Results and discussion

Cole–Cole plots were drawn from the real and imaginary values of permittivity. They are semicircular in nature and exhibit a broader dispersion. The centre of the semicircle lies below the real axis (figure 2). This is indicative of broadening of relaxation. From Cole–Cole plots dispersion parameters like static dielectric constant (ε_s) and optical dielectric constant (ε_∞) are obtained directly by noting the real axes intercepts [18]. Parameters like average relaxation time (τ_0), distribution parameter (α) and molecular relaxation time (τ) are also evaluated by employing equations (3)–(5). These dispersion parameters are tabulated and depicted in table 1.

The variation of optical dielectric constant with temperature is shown in figure 3. It can be seen that as temperature rises, optical dielectric constant decreases. This is due to the increase in the broadening of distribution of relaxation time with an increase in temperature.

Static dielectric constant increases with rise in temperature and is shown in figure 4. This is because of the enhancement in polarization with an increase in temperature. Reports exist

in the literature wherein similar behaviour has been noticed for other materials too [28].
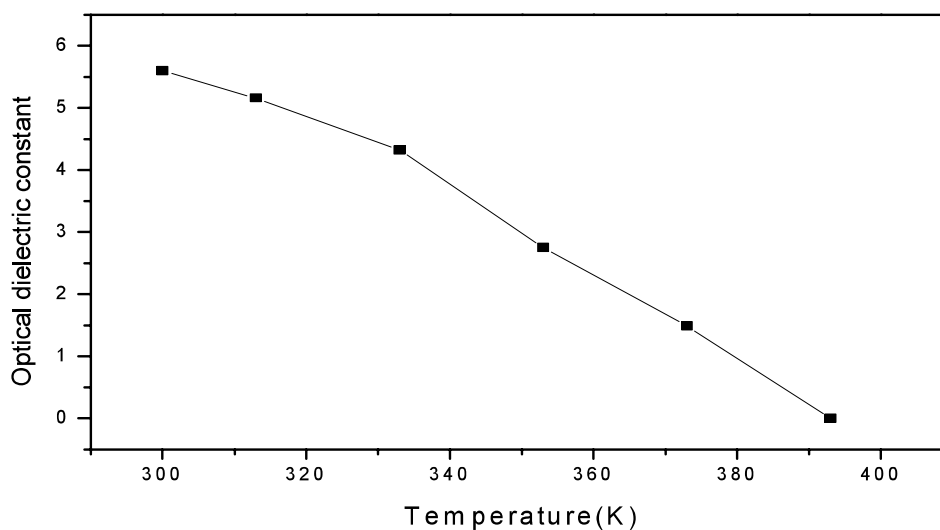
From Cole–Cole plots (figure 2) it is evident that the centres of the circular arcs lie below the real axis, which is an indication of the distribution of relaxation time (for single relaxation time the plot is a semicircle with the centre on the real axis). This is in agreement with various polymers exhibiting broader relaxation due to a wide range of forces which are required to restrain the orientation of segmental dipoles [21]. According to the bistable model proposed by Frolich, there exist two equilibrium positions for the dipole [22]. These positions are determined by the minima of the potential well and are separated by the potential hill. If the charged particle possesses enough energy to cross over the potential hill, then there is dielectric relaxation and this is associated with a single relaxation time [22]. However, a molecule in a solid might possess more than one equilibrium position corresponding to the minima of potential energy and separated by more than one potential hill. A charged particle under activation, while crossing these potential hills, gives rise to multiple relaxation times. Such a phenomenon is characterized by a distribution of the relaxation time. This is evidence of the existence of multiple equilibrium states in the case of cobalt phthalocyanine.

In the case of cobalt phthalocyanine, with increase in temperature, charged particles acquire enough thermal energy to cross over the potential hills. This is one reason for the increase in the spreading factor with increase in temperature. The variation of distribution parameter (spreading factor) is depicted in figure 5. It can be seen that the spreading factor increases with increase in temperature. The variation pattern

Table 1. Dispersion parameters obtained from Cole–Cole fit of dielectric data at various temperatures.

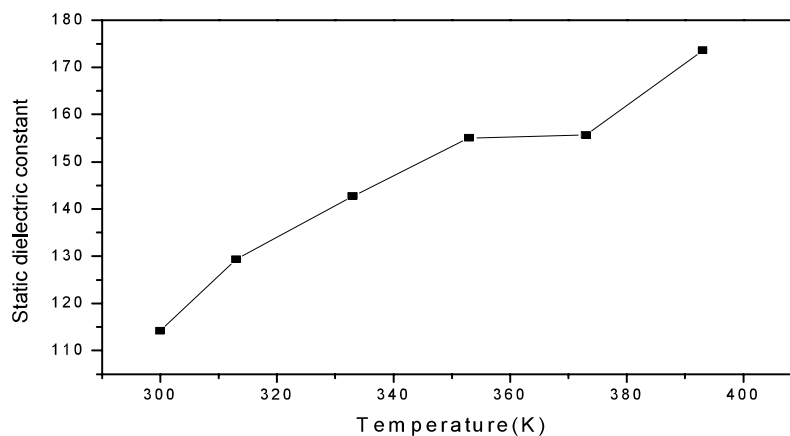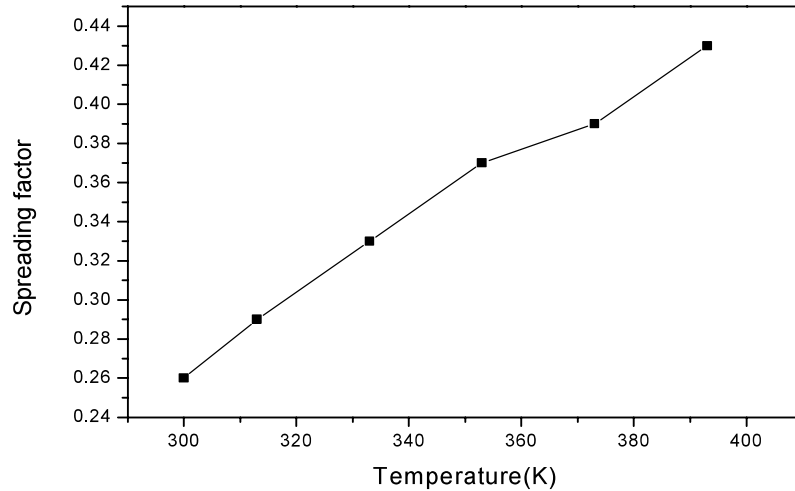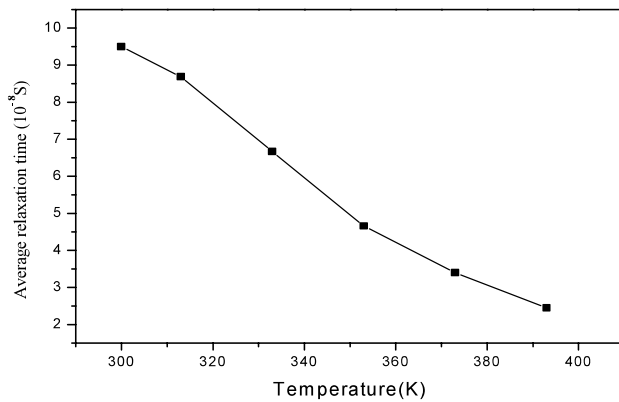| Temperature (K)	ε_∞	ε_s	α	τ_0 $(10^{-8}\,s)$	τ $(10^{-8}\,s)$
300	5.6	114.19	0.26	9.5	6.3
313	5.16	129.31	0.29	8.69	5.82
333	4.32	142.75	0.33	6.67	4.5
353	2.75	155.1	0.37	4.66	3.15
373	1.49	155.67	0.39	3.4	2.31
393	0	173.63	0.43	2.45	1.67

Figure 3. Variation of optical dielectric constant with temperature.
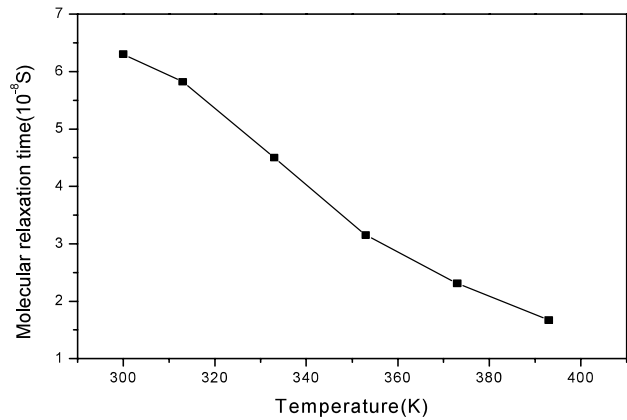

Figure 4. Variation of static dielectric constant with temperature.

Figure 5. Temperature dependence of spreading factor.

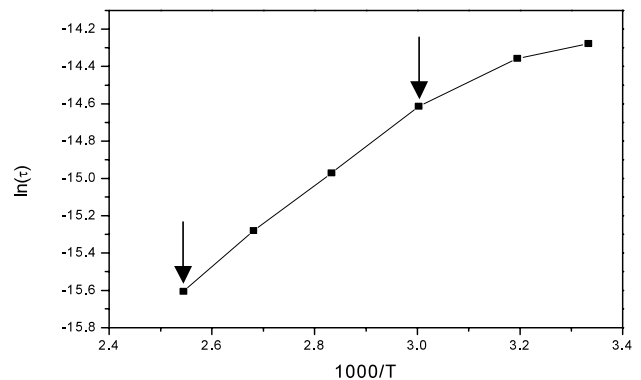**Figure 6.** Variation of average relaxation time with temperature.

Figure 7. Variation of molecular relaxation time with temperature.

observed for cobalt phthalocyanine is in agreement with that of several other reports [28–30]. It is to be noted that the evaluation of spreading factor is seldom evaluated for polymers or seldom reported in the literature. This seems to be an attempt for the first time. Schonau and Redfern [28] observed the same behaviour in the case of proustite while Rychetsky and others [29] noticed similar characteristics in a system consisting of PLZT relaxor. Also Sentiirk [30] pointed out the same in strontium barium niobate. However Yasuda *et al* [31] did not observe such a behaviour in the case of cadmium niobate. The average relaxation time as well as the molecular relaxation time is plotted against temperature separately and they are depicted in figures 6 and 7, respectively. In both these cases there is a decrease with increase in temperature. This behaviour is in accordance with the Debye theory of dipolar orientation [17]. The rise in temperature causes a reduction in mean time of stay of ionic dipoles which in turn causes the relaxation time to decrease [32].

The dielectric relaxation is related to the thermally activated process wherein the relaxation time is of the form

$$\tau = \tau_\infty \exp(E_0/kT), \qquad (6)$$

where τ_∞ is the relaxation time at infinite temperature and E_0 is the activation energy.

Figure 8. Variation of $\log \tau$ with $1000/T$ for the calculation of activation energy. (The linear portion is marked with arrow marks.)

It is evident from this relation that as temperature increases relaxation time decreases. Activation energy was calculated from the slope of the $\ln(\tau)$ versus $1000/T$ (figure 8). The activation energy calculated for cobalt phthalocyanine is found to be 0.185 eV. This is in good agreement with that of the reported values obtained from dc conductivity measurements [17].

5. Conclusion

The graphical method of the Cole–Cole diagram was successfully employed to generate dispersion parameters in the temperature range 300–393 K for cobalt phthalocyanine for the first time. The average relaxation time and molecular relaxation time are approximately of the same order ($\sim 10^{-8}$ s). The temperature dependence of the spreading factor was successfully explained by the multiple equilibrium state model (model with more than two equilibrium positions). The broadening of relaxation time confirmed the presence of enhanced inter-molecular interaction among the cobalt phthalocyanine tetramers. Extrapolation using the Cole–Cole method is an added advantage of this graphical technique to predict the dielectric permittivity at very high frequencies. The activation energy of the polymer sample is 0.185 eV which is in good agreement with the reported value [17].

Acknowledgments

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