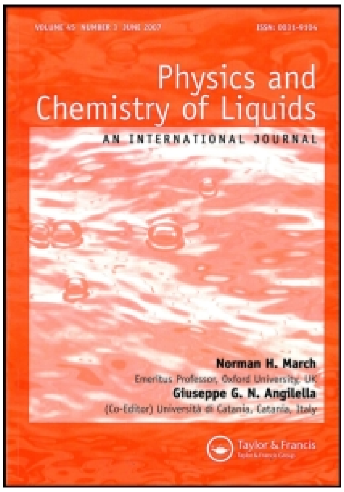

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Shukla, J. P. , Misra, Rajni , Singh, Amar , Gupta, Manisha and Saxena, M. C.(1989) 'Dielectric Relaxation Study from Polarisability Data', Physics and Chemistry of Liquids, 19: 4, 241 — 251
To link to this Article: DOI: 10.1080/00319108908028446
URL: http://dx.doi.org/10.1080/00319108908028446

Phys. Chem. Liq., 1989, Vol. 19, pp. 241-251
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DIELECTRIC RELAXATION STUDY FROM POLARISABILITY DATA

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(Received 3 October 1988)

An analysis of the dielectric data using the polarisability plots have been carried out in our earlier paper [Current Sci. India 15 (1982) 695]. The polarisability equations proposed in our earlier paper have been modified by introducing a correction term. The equations of Higasi and Budo to evaluate relaxation time have been changed from using slope and dielectric data respectively to that using polarisability data. These proposed and modified equations have been applied to a number of systems for evaluating the relaxation parameters. The results obtained from the modified equations are in better agreement. It has also been confirmed from the present investigation that the angular frequency 'ω' manifests as 'ωC'

$$C = \frac{1 - p_0}{1 - p_\infty} \text{ or } C = \frac{1 - \alpha_0}{1 - \alpha_\infty}$$

KEY WORDS: Cole-Cole plot, polarizability plot.

INTRODUCTION

The study of dielectric dispersion behaviour of molecules requires the evaluation of permittivity data over a wide range of frequency, temperature and concentration. To evaluate the relaxation time, the dielectric data are analysed by Cole-Cole Plot, Cole-Davidson plot or polarisability plot. The C-C plot is the representation of ε'' against ε' or a'' against a' on the graphical paper and so is the C-D plot. Scaife suggested that the graphical representation of real and imaginary parts of complex polarisability $\alpha^*(\omega)$ instead of $\varepsilon'' - \varepsilon'$ representation would be better representation and yield better results. We had proposed some equations to calculate the relaxation time using polarisability data for some molecules in our earlier paper[1] and had obtained a good agreement with the results of slope data. Since limited study has been made in this direction we have extended our work further to test the applicability of the proposed equations. In the present investigation the slope data[2-9] have been utilized to calculate the real and imaginary parts of complex polarisability function

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$p^*(\omega)$. The real and imaginary parts of complex polarisability $\alpha^*(\omega)$ have been calculated using dielectric data from literature[10–12]. The equations in terms of polarisability, analogous to Higasi's equation of single frequency concentration variation method and Budo's equations for multiple frequency data analysis have been proposed to calculate the most probable relaxation time and group and molecular relaxation time. The results seem to demand a new, correction factor (A) in our previously proposed equations to reach closer agreement with the values using slope data and dielectric data.

(*A*) *Single Microwave Frequency Data Analysis*

For explaining the dielectric phenomenon, Debye proposed an equation, which is restricted to hold only in liquids and in the dilute solutions of polar components in non-polar solvents i.e.;

$$\frac{\varepsilon^* - n^2}{\varepsilon_0 - n^2} = \frac{1}{(1 + j\omega\tau)} \tag{1}$$

For the representation of non-Debye type of absorption as in the case of long chain molecules, Cole–Cole used an empirical factor in the dispersion function which takes the form:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (j\omega\tau)^{1-\alpha}};\ 0 < \alpha < 1 \text{ and } \alpha = 0 \Rightarrow \text{Debye function} \tag{2}$$

This function results in the parametric equation of a circle of plot of ε'' vs. ε'. The relaxation time may be calculated using the equation

$$\frac{v}{u} = (\omega\tau)^{1-\alpha} \tag{3}$$

where 'v' and 'u' are the distances of the points from ε_0 and ε_∞ points on the ε' axis respectively. Thus the frequency variation method essentially deals with the plotting of ε' vs. ε''. The curve results either as semi-circular or as skewed arc.

Later on, it was pointed out by Franklin *et al.*[13] that the plot of slopes a' vs. a'' in the complex plane is exactly similar to ε' vs. ε'' plot and a similar approach is adopted for the evaluation of relaxation time of polar substances in non-polar solvent.

The reliability that the slopes a' and a'' can be used to calculate the relaxation time from dilute solution studies has been assessed by Higasi *et al.* It led Higasi[14] to formulate the equations to calculate the relaxation time at a single frequency, given by,

$$\tau_{\mathrm{OH}} = \frac{1}{\omega}\left(\frac{A^2 + B^2}{C^2}\right)^{1/2(1-\alpha)} \tag{4a}$$

where

$$1 - \alpha = \frac{2}{\pi}\tan^{-1}\frac{A}{B} \tag{4b}$$

and

$$\begin{aligned} A &= a''(a_0 - a_\infty) \\ B &= (a_0 - a')(a' - a_\infty) - a''^2 \\ C &= (a' - a_\infty)^2 + a''^2 \end{aligned} \tag{5}$$

Higasi *et al.*[15] analysed the permitivity data in terms of two independent relaxation processes analogous to the equations

$$\tau_{(1)} = \frac{1}{\omega} \frac{a''}{(a' - a_\infty)} \tag{6a}$$

$$\tau_{(2)} = \frac{1}{\omega} \frac{(a_0 - a')}{a''} \tag{6b}$$

The Cole-Cole method of analysing dielectric data may be replaced by the use of polarisability plot as suggested by Scaife[16], because polarisability is a good measure of intrinsic property of a substance. Here, the imaginary coordinate of complex function $p^*(\omega)$ is plotted against its real coordinate. Since the polarisability plot is a bilinear transformation of C-C plot, the shape remains the same as in the case of C-C plot and all the attractive features of C-C plot may well turn out to be the most important features of p′-p″ plot also. As polarisability plot provides more stringent test than C-C plot, there seems to be justification of analysing the dielectric data with the known polarisability data.

We have proposed[1] a method to calculate the relaxation time using polarisability function plots. The plot of p' vs. p'' had been found to be semicircular arc and the relaxation time was calculated using the equation

$$\frac{v}{u} = (C\omega\tau_p)^{1-\alpha} \quad \text{where} \quad C = \frac{1 - p_0}{1 - p_\infty} \tag{7}$$

We also have proposed equations to evaluate the relaxation times associated with the group and the molecular processes separately using the following equations.

$$\tau_{p(1)} = \frac{1}{C\omega} \frac{p''}{p' - p_\infty} \tag{8a}$$

and

$$\tau_{p(2)} = \frac{1}{C\omega} \frac{p_0 - p'}{p''} \tag{8b}$$

This paper now attempts to evaluate $\tau_{p(\mathrm{OH})}$ i.e.; the most probable relaxation time using p' and p'' etc. corresponding to Higasi equation instead of a' and a'' etc. Hence, the new equation for polarisability data which is analogous to Higasi's equation

$$\tau_{p(\mathrm{OH})} = \frac{1}{\omega C} \left(\frac{A_p^2 + B_p^2}{C_p^2} \right)^{1/2(1-\alpha_p)} \tag{9a}$$

where

$$(1 - \alpha_p) = \frac{2}{\pi} \tan^{-1} \frac{A_p}{B_p} \tag{9b}$$

and

$$A_p = p''(p_0 - p_\infty)$$

$$B_p = (p_0 - p')(p' - p_\infty) - p''^2$$

$$C_p = (p' - p_\infty)^2 + p''^2$$

In order to check the validity of Eqs. (7), (8) and (9) calculations have been carried out for twenty seven system in varying media and at different temperature. The slope data for all these systems have been taken from literature[2–9].

The most striking factor that comes to light is that almost for all compounds $\tau_{OH} > \tau_{p(OH)}$, but at the same time $\tau_{p(1)}$, $\tau_{p(2)}$ and $\tau_{p(0)} > \tau_{(1)}$, $\tau_{(2)}$ and $\tau_{(0)}$ respectively. Our previous results[1] also lead to the same inequality. It thus appeared interesting to carryout the analytical treatment for the exhibited behaviour.

We therefore proceed as below to evaluate the relaxation time from polarisability plot

From Figure 1,

$$\frac{v^2}{u^2} = \frac{(p' - p_0)^2 + p''^2}{(p' - p_\infty)^2 + p''^2}$$

i.e.,

$$\frac{v^2}{u^2} = \frac{\left[1 - \left(\frac{p' - p_\infty}{p_0 - p_\infty}\right)\right]^2 + \frac{p''^2}{(p_0 - p_\infty)^2}}{\left[\frac{p' - p_\infty}{p_0 - p_\infty}\right]^2 + \frac{p''^2}{(p_0 - p_\infty)^2}} \tag{11}$$

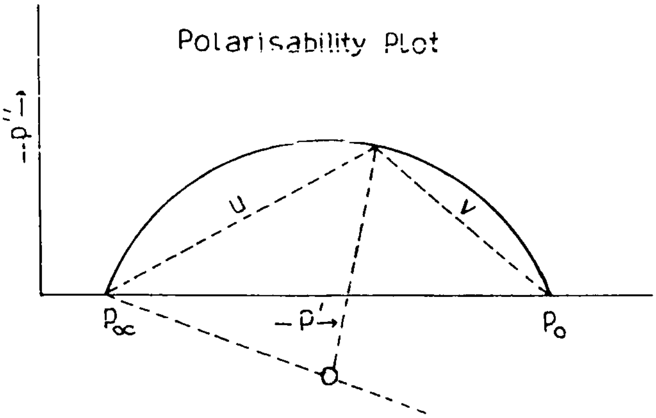

Figure 1

Now making use of following Eqs. (12) and (13)

$$p_0 = \frac{a_0 - 1}{a_0 + 2}, \quad p' = \frac{a'^2 + a''^2 + a' - 2}{(a' + 2)^2 + a''^2}$$
$$p_\infty = \frac{a_\infty - 1}{a_\infty + 2}, \quad p'' = \frac{3a''}{(a' + 2)^2 + a''^2} \tag{12}$$

and

$$a^* = a_\infty + \frac{a_0 - a_\infty}{1 + (j\omega\tau'_p)^{1-\alpha}} \tag{13}$$

finally, we get

$$\frac{v}{u} = \left(\frac{a_\infty + 2}{a_0 + 2}\right)(\omega\tau'_p)^{1-\alpha}$$

or

$$\frac{v}{u} = C(\omega\tau'_p)^{1-\alpha} \tag{14}$$

where

$$C = \frac{1 - p_0}{1 - p_\infty}$$

In order to bring an equivalence in (7) and (14) we introduce a correction factor $A = (C^{-\alpha/1-\alpha})$ such that

$$\tau'_p = A \cdot \tau_p$$

Since $\tau_{OH} > \tau_{p(OH)}$, has been observed it appears reasonable to introduce such a correction factor with $\tau_{p(OH)}$ value as:

$$\tau'_{p(OH)} = A\tau_{p(OH)} \tag{15}$$

Further, the polarisability function being the bilinear transform of C-C functions, (hence having the same phase as of C-C plot), the equation corresponding to the polarisability function should be,

$$p^* = p_0 + \frac{p_0 - p_\infty}{1 + (i\omega C\tau'_p)^{1-\alpha}}$$

or,

$$p^* = p_0 + \frac{p_0 - p_\infty}{1 + (iA\omega C\tau_p)^{1-\alpha}} \tag{16}$$

This on separating real and imaginary parts results into:

$$\frac{p' - p_\infty}{p_0 - p_\alpha} = \frac{1}{1 + \omega^2 C^2 \tau_p^2 A^2} \tag{17a}$$

and

$$\frac{p''}{p_0 - p_\infty} = \frac{\omega C \tau_p A}{1 + \omega^2 C^2 \pi_p^2 A^2} \qquad (17b)$$

Rewriting Eq. (17a) as:

$$1 - \frac{p_0 - p'}{p_0 - p_\infty} = \frac{1}{1 + \omega^2 C^2 \tau_p^2 A^2}$$

or

$$\frac{p_0 - p'}{p_0 - p_\infty} = \frac{\omega^2 C^2 \tau_p^2 A^2}{1 + \omega^2 C^2 \tau_p^2 A^2} \qquad (17c)$$

Dividing (17b) by (17a),

$$\tau'_{p(1)} = \frac{1}{A(\omega C)} \cdot \frac{p''}{p' - p_\infty}$$

or

$$\tau'_p(1) = \frac{1}{A} \tau_{p(1)} \qquad (18a)$$

Dividing (17c) by (17b):

$$\tau'_{p(2)} = \frac{1}{A(\omega C)} \frac{p_0 - p'}{p''}$$

or

$$\tau'_{p(2)} = \frac{1}{A} \tau_{p(2)} \qquad (18b)$$

Combining (18a) and (18b);

$$\tau'_{p(0)} = \sqrt{\tau'_{p(2)} \cdot \tau'_{p(1)}} = \frac{1}{A} \cdot \tau_{p(0)} \qquad (18c)$$

Thus, the introduction of the correction factor A, which is analytically true, no doubt, accounts for the inequalities pointed out earlier as it is multiplicative with τ_p and $\tau_{p(\mathrm{OH})}$ while is divisor with $\tau_{p(1)}$, $\tau_{p(2)}$ and $\tau_{p(0)}$. The results obtained by the introduction of 'A' in Eqs (8) and (9) would be expected to yield parameter in agreement with Higasi's results obtained using (4) and (6) directly.

Results The values τ_{OH}, $\tau_{p(\mathrm{OH})}$, $\tau_{(1)}$, $\tau_{(2)}$, $\tau_{(0)}$, $\tau_{p(1)}$, $\tau_{p(2)}$, $\tau_{p(0)}$ along with corrected values $\tau'_{p(\mathrm{OH})}$, $\tau'_{p(1)}$, $\tau'_{p(2)}$ and $\tau'_{p(0)}$ for all compounds analysed are given in Table 1.

Discussion As can be seen from Table 1, α-Naphthaldehyde yields the relaxation time value of $\tau_{p(\mathrm{OH})}$ of 21.0 ps which slightly differ from τ_{OH} value of 26.2 ps, but $\tau'_{p(\mathrm{OH})}$ value of 26.1 ps is closer to τ_{OH}. Similarly $\tau'_{p(1)}$ of 16.6 ps is in close agreement to $\tau_{(1)}$

value of 17.0 ps instead of $\tau_{p(1)}$ value of 21.0 ps. $\tau'_{p(2)}$ value of 30.4 ps is close to $\tau_{(2)}$ value of 29.4 ps while $\tau_{p(2)}$ value 38.4 ps is much different from $\tau_{(2)}$. $\tau'_{p(0)}$ value of 22.5 ps is in close agreement to 22.3 ps value of $\tau_{(0)}$. $\tau_{p(0)}$ value of 21.0 ps is a little less than $\tau_{(0)}$.

An observation of the data, evaluated, (Table 1) reveals that all the remaining system show similar trend. This strongly favours the insertion of the correction factor. The correction term (A) in the denominator of the expressions for $\tau'_{p(1)}$, $\tau'_{p(2)}$ and $\tau'_{p(0)}$ and in the numerator of the expression for $\tau'_{p(\mathrm{OH})}$ confirms the opposite trend i.e., $\tau_{\mathrm{OH}} > \tau_{p(\mathrm{OH})}$, $\tau_{p(1)} > \tau_{(1)}$, $\tau_{p(2)}$ and $\tau_{p(0)} > \tau_{(0)}$.

The difference $[\tau'_{p(2)} - \tau'_{p(1)}] > [\tau_{p(2)} - \tau_{p(1)}]$ while at the same time $\tau'_{p(0)} \approx \tau_{(0)}$. The polarisability data analysis provides a good resolution and the method can thus be used for resolving the relaxation mechanisms[1].

(*B*) *Multiple Frequency Data Analysis*

The dielectric constant, a complex quantity $\varepsilon^*(\omega)$ is given by Debye's equation

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

where

$$\varepsilon' = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (\omega\tau)^2} \quad \text{and} \quad \varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2} \tag{19}$$

The polarisability also becomes a complex function and is written as

$$\alpha^* = \alpha' - i\alpha'' = \frac{\varepsilon^* - 1}{\varepsilon^* + 2} \tag{20}$$

According to Scaife the complex polarisability may be written as:

$$\alpha^* = \alpha_\infty + \frac{\alpha_0 - \alpha_\infty}{1 + (i\omega\tau)^{1-\alpha}} \tag{21}$$

Substituting $\varepsilon^* = \varepsilon' - i\varepsilon''$ in Eq. (21), the real (α') and imaginary (α'') parts of polarisability function α^* may be written as:

$$\alpha' = \frac{\varepsilon'^2 + \varepsilon''^2 + \varepsilon' - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} \quad \text{and} \quad \alpha'' = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} \tag{22}$$

Budo's equation[17] for resolution of the dielectric mechanism using frequency variation method are given by

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{C_1}{1 + (\omega\tau_1)^2} + \frac{C_2}{1 + (\omega\tau_2)^2} \tag{23}$$

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{C_1(\omega\tau_1)}{1 + (\omega\tau_1)^2} + \frac{C_2\cdot(\omega\tau_2)}{1 + (\omega\tau_2)^2}$$

where all symbols have their usual meanings.

Table 1 Relaxation time (τ in ps) using Equations 4, 6, 8, 9, 15 and 18.

Systems	*Using slope data*				*Using polarisability data*				*Using corrected polarisability equation*			
	$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$	$\tau_{(OH)}$	$\tau_{p(1)}$	$\tau_{p(2)}$	$\tau_{p(0)}$	$\tau_{p(OH)}$	$\tau'_{p(1)}$	$\tau'_{p(2)}$	$\tau'_{p(0)}$	$\tau'_{p(OH)}$
1. α-Naphthylamine	8.4	15.1	11.3	9.3	8.8	17.2	12.3	8.6	8.1	15.8	11.3	9.3
2. α-Naphthaldehyde	17.4	29.4	22.3	26.2	21.0	38.4	21.0	21.0	16.6	30.4	22.5	26.1
3. β-Naphthaldehyde	17.4	30.6	23.1	27.7	22.0	42.8	30.7	21.2	16.5	32.0	23.0	28.4
4. α-Chloronaphthalene	18.4	18.5	18.5	18.5	18.4	18.6	18.5	18.4	18.4	18.5	18.4	18.6
5. α-Bromonaphthalene	20.5	22.3	21.4	21.8	21.0	22.8	21.9	21.5	20.7	22.4	21.6	21.8
6. α-Naphthylamine												
(at 20°C)	6.7	22.9	12.4	8.1	7.7	35.2	16.4	5.3	5.3	24.0	11.2	8.1
(at 40°C)	5.9	23.3	11.7	5.9	6.9	28.4	14.1	4.3	5.0	21.1	10.3	5.9
(at 60°C)	4.8	15.9	8.8	4.2	5.2	23.8	8.1	3.1	4.0	18.2	6.2	4.2
7. β-Naphthylamine												
(at 20°C)	10.5	21.6	15.0	13.5	12.0	31.3	19.4	10.1	11.1	28.8	17.8	13.1
(at 40°C)	8.7	16.5	12.0	9.6	9.5	23.4	14.9	7.1	9.0	22.2	14.1	9.5
(at 60°C)	7.2	9.5	8.3	7.2	7.8	12.1	9.7	8.8	7.6	11.7	9.4	7.2
8. N-Phenyl 1,Naphthylamine in benzene												
(at 20°C)	8.2	24.6	14.3	10.9	9.0	28.6	16.1	9.3	8.0	25.7	15.0	11.1
(at 40°C)	6.3	19.9	11.2	6.6	6.6	23.8	12.6	5.5	6.1	21.8	11.5	6.5
(at 60°C)	5.3	15.8	9.2	4.8	5.5	19.0	10.2	4.1	5.2	17.9	9.6	4.7
9. N-Phenyl 2,Naphthylamine in decaline												
(at 20°C)	7.7	29.0	14.9	12.6	8.3	32.7	16.5	9.9	7.8	30.9	15.6	11.9
(at 40°C)	7.4	27.2	14.2	10.6	7.9	30.4	15.5	9.2	7.6	29.4	15.0	10.7
10. N-Phenyl 2,Naphthylamine in benzene												
(at 20°C)	5.9	34.2	14.2	8.9	6.8	43.7	17.2	6.2	6.4	41.3	16.2	9.2
(at 40°C)	5.7	24.8	11.2	6.2	6.2	31.6	14.0	4.7	6.0	30.6	13.5	6.3
(at 60°C)	5.2	15.3	8.9	4.7	5.4	19.4	10.2	3.9	5.4	19.3	10.1	4.6

11. 2,6 Dimethylanisole												
(at 20°C)	18.0	24.3	20.9	22.1	19.3	26.6	22.7	20.7	17.8	24.5	20.9	22.1
(at 40°C)	15.3	18.4	16.7	16.7	15.9	19.6	17.6	16.2	15.0	18.5	16.9	16.8
(at 60°C)	13.5	14.8	14.1	13.1	13.7	15.0	14.3	13.7	13.1	14.4	13.8	13.9
12. 3,5 Dimethylanisole												
(at 20°C)	11.6	17.8	14.4	13.6	12.5	21.0	16.2	12.4	11.4	19.1	14.7	13.6
(at 40°C)	10.3	12.7	11.5	10.7	10.5	13.8	12.1	10.3	9.9	13.1	11.4	10.7
(at 60°C)	8.5	10.9	3.7	8.7	8.7	11.8	10.1	8.4	8.3	11.4	8.7	8.6
13. Bis-Chloromethyldurene	39.4	72.3	53.4	53.6	46.9	110.5	71.8	40.4	35.3	83.2	54.2	53.4
14. α-α'dichloro, p-xylene												
(at 20°C)	4.9	9.9	7.0	4.4	5.2	19.5	10.0	3.5	4.2	15.7	8.1	4.5
(at 40°C)	5.1	6.2	5.6	5.0	5.3	8.0	6.5	4.9	4.5	6.9	5.5	5.1
(at 60°C)	3.1	5.7	4.2	2.7	3.1	9.6	5.5	2.5	2.9	9.0	5.1	2.7
15. Flurobenzene	5.8	7.8	6.7	5.7	5.9	10.0	7.7	5.3	5.6	9.4	7.3	5.6
16. Dibenzoylmethane	12.5	15.9	14.1	13.7	13.3	19.4	16.1	12.5	8.3	17.7	14.7	13.7
17. Octanoyl Chloride	11.1	12.9	12.0	11.5	11.5	16.0	13.6	10.8	10.7	14.5	12.7	11.6
18. Undecanoyl Chloride	11.8	15.5	13.5	13.0	12.7	20.6	16.2	11.6	11.5	18.6	14.6	12.9
19. Lauroyl Chloride	12.5	16.9	14.5	14.1	13.6	22.5	17.4	12.4	11.9	19.7	15.3	14.2
20. Benzoyl Acetone	8.6	16.5	11.9	9.8	14.2	33.1	21.7	6.9	9.9	23.1	15.2	9.9
21. Ethyltrichlororoacetate in n-heptane	8.0	19.0	12.3	15.1	9.1	27.9	15.9	7.3	5.2	16.1	9.2	12.6
22. N-N'Dimethyl, p-methyl aniline	16.3	24.3	19.8	24.9	17.7	26.8	21.8	19.9	16.3	24.7	20.1	21.5
23. dl-Campher												
(at 40°C)	10.0	10.2	10.1	10.0	10.0	10.7	10.4	10.0	10.0	10.5	10.2	10.1
(at 60°C)	7.9	9.3	8.5	7.9	8.2	13.9	10.7	7.5	7.6	12.9	9.9	8.0
24. Adamantane Bromide	16.9	15.4	16.1	16.1	16.4	13.6	14.9	15.6	15.8	13.1	14.4	16.2
25. Ethyl α-Bromobutyrate	6.1	21.6	11.5	7.1	7.3	41.6	17.4	3.9	4.0	22.8	9.5	7.1
26. Ethyltrichloroacetate (in benzene)	8.9	30.9	16.6	17.3	11.9	55.0	25.6	8.6	6.0	27.5	12.8	17.1
27. Adamantane Chloride	15.2	15.6	15.4	15.4	14.7	15.5	14.8	15.1	14.0	15.4	14.6	15.3

In analogy with the equations modified for polarisability data in our previous section, it has been proposed that Eq. (23) will be modified for polarisability data as:

$$\begin{aligned} \frac{\alpha' - \alpha_\infty}{\alpha_0 - \alpha_\infty} &= \frac{C_1}{1 + (\omega C \tau_{p_1})^2} + \frac{C_2}{1 + (\omega C \tau_{p_2})^2} \\ \frac{\alpha''}{\alpha_0 - \alpha_\infty} &= \frac{C_1 \cdot \omega C \tau_{p_1}}{1 + (\omega C \tau_{p_1})^2} + \frac{C_2 \cdot \omega C \tau_{p_2}}{1 + (\omega C \tau_{p_2})^2} \end{aligned} \tag{24}$$

where $C = 1 - \alpha_0/1 - \alpha_\infty$ and c_1 and c_2 are the weight factors associated with the relaxation processes. The values of relaxation times τ_{p_1} and τ_{p_2} evaluated using Eq. (24) have been found close to the reported values but generally a little higher for the systems which have sufficiently high values of distribution parameter (α). So on the basis of our previous study a correction factor $A = C^{-\alpha/1-\alpha}$ was introduced here also. Thus Eq. (24) takes the form,

$$\frac{\alpha' - \alpha_\infty}{\alpha_0 - \alpha_\infty} = \frac{C_1}{1 + (\omega C \cdot A \tau_{p_1})^2} + \frac{C_2}{1 + (\omega C \cdot A \tau_{p_2})^2} \tag{25a}$$

$$\frac{\alpha''}{\alpha_0 - \alpha_\infty} = \frac{C_1 \cdot \omega C \tau_{p_1} A}{1 + (\omega C A \tau_{p_1})^2} + \frac{C_2 \cdot \omega C \tau_{p_2} A}{1 + (\omega C \cdot A \tau_{p_2})^2} \tag{25b}$$

On combining Eqs. (25a) and (25b) we get

$$\frac{1 - X}{Y \omega C} = A(\tau_{p_1} + \tau_{p_2}) - \frac{X \omega C}{Y} A^2 \tau_{p_1} \tau_{p_2} \tag{26}$$

Table 2 Relaxation Times (τ in ps) calculated using (24) and (25).

	Temp.	*Using Eq.* (24)		*Using Eq.* (25)		*Using Budo's Eq.* (*Rpted*)	
	(°C)	τ_{p_1}	τ_{p_2}	τ'_{p_1}	τ'_{p_2}	τ_1	τ_2
1. 1,5 Dicyanopentane	30	30.8	10.4	28.9	9.8	28.6	8.6
	45	26.0	7.0	24.2	6.5	23.8	6.8
	60	21.8	6.2	20.5	5.8	18.9	4.9
2. 1,6 Dicyanohexane	30	37.9	10.1	34.9	9.3	33.0	7.5
	45	30.2	8.0	27.9	7.4	27.6	6.5
	60	26.0	6.0	23.4	5.6	22.9	4.8
3. 1,7 Dicyanoheptane	30	39.1	9.4	35.9	8.6	35.1	7.6
	45	31.7	7.3	28.9	6.7	28.7	6.0
	60	26.2	5.3	24.0	4.8	23.8	4.8
4. Methylmercaptoacetate	30	24.9	4.1	22.6	3.7	24.0	3.6
	45	23.4	3.1	20.9	2.8	22.2	2.9
	60	22.8	2.2	20.1	1.9	21.0	2.1
5. Methylcyanoacetate	30	38.0	10.0	36.3	9.5	38.0	8.4
	45	36.9	7.1	35.0	6.7	35.6	6.6
	60	24.9	4.1	22.6	3.7	22.5	4.9
6. Ethyltrichloroacetate in cyclohexane	25	31.1	5.0	30.9	4.9	28.9	5.9
7. Ethyltrichloroacetate in p-xylene	25	38.1	6.4	37.7	6.3	35.9	6.4
8. Ethyltrichloroacetate in p-dioxane	25	46.0	3.0	44.9	3.0	43.5	4.8

where 'X' and 'Y' refer to left hand side of Eqs. (25a) and (25b) respectively. Thus, simply by plotting $(1 - X/Y\omega C)$ vs. $(X\omega C/Y)$ a straight line is obtained. $A(\tau_{p_1} + \tau_{p_2})$ is cutoff value of Y axis and $A^2\tau_{p_1}\tau_{p_2}$ is slope of that line, hence by knowing intercept $A(\tau_{p_1} + \tau_{p_2})$ and slope $(A^2\tau_{p_1}\tau_{p_2})$, this time the corrected values of group $(\simeq\tau_{p_2})$ and molecular $(\simeq\tau'_{p_1})$ relaxation times can be evaluated.

RESULTS AND DISCUSSION

The relaxation times evaluated using Eqs. (24) and (25) along with literature values are reported in Table 2.

The molecular and group relaxation values evaluated using Eq. (24) for compound 1,5-dicyanopentane at temp. 30°C having been found as $\tau_{p_1} = 30.8$ ps and $\tau_{p_2} = 10.4$ ps. But the values ($\tau'_{p_1} = 28.6$ and $\tau'_{p_2} = 9.8$) ps evaluated using Eq. (25) having a correction term (A) show excellent agreement with the literature values. Similar trend was observed in the previous section. As may be seen from the table containing relaxation time values, the values for all compounds studied here obtained from polarisability equations without having correction term are higher than those in the literature but these values become closer on the introduction of the correction term. Thus these results indicate that the Eq. (25) with polarisability data is more applicable for calculating the reflexation time than Eq. (24).

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