

on a low iodide diet for 3 days then divided into groups consisting of four rats in each group. The animal in each group received an intraperitoneal injection of 1 ml of either a blank (0.9% NaCl), thiouracil, or one of the test compounds. One hour later $1 \mu\text{Ci}$ of $\text{Na } ^{131}\text{I}$ (carrier free) was injected intraperitoneally. Three hours after the injection of ^{131}I the animals were sacrificed and the thyroid were removed. The whole lobes were placed in ground glass homogenizing tubes and counted in Nuclear-Chicago well-scintillation counter to determine total thyroid uptake. The whole lobes were then homogenized in 1 ml of 0.05 M barbital buffer (pH 8.6) containing 1.0×10^{-5} M thiouracil. One ml of cold 20% trichloroacetic acid (TCA) was added and the homogenate was centrifuged. The precipitate was washed twice with 1 ml of cold 10% TCA. The original supernatant and the two washes were combined and the radioactivity was determined. The ^{131}I in this fraction indicated the concentration of inorganic ^{131}I or TCA-soluble ^{131}I . The washed precipitate was counted in the homogenizing tube. The radioactivity in this fraction indicated the PB ^{131}I (protein-bound iodine) or the TCA-precipitate ^{131}I . The counts were all corrected for counting efficiency and are expressed as disintegration per minute.

All compounds were dissolved in saline for injection. Thiouracil was dissolved with heating to 50°C .

All compounds were assayed at concentration equimolar to 0.5 mg of thiouracil ($3.9 \mu\text{mole}$) and the biological effect was noted. Table 4 summarizes the observations made with compounds 1 to 12.

It is evident from the results of pharmacological studies (shown in table 4) that none of the above compounds appears to be more potent than thiouracil.

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STUDY OF DIELECTRIC RELAXATION PROCESSES USING AN APPROACH BASED ON THE POLARIZABILITY FUNCTION PLOTS

AMAR SINGH, S. K. SAXENA* AND M. C. SAXENA

Physics Department, Lucknow University, Lucknow 226 007, India.

* Permanent address, Department of Physics, D.B.S. College, Kanpur, India.

ABSTRACT

A new method for calculating the most probable relaxation time and distribution parameter for polar molecules using the polarizability function plots has been proposed. The relaxation times by this method agree well with the relaxation times obtained using Higasi and others and by the Cole-Cole method. It has been concluded that the angular frequency ω used in the dielectric data manifests itself as $C\omega$ ($C = 1 - p_0 / 1 - p_\infty$) when identical equations relating to the polarizability are taken in place of the usual equations. It has also been observed that the molecular and group processes are better resolved, if suitably proposed equations pertaining to polarizability are employed to separate out the two processes at a single frequency.

INTRODUCTION

THE frequency variation methods^{1,2} essentially consist of plotting the dielectric constant ϵ' vs dielectric loss ϵ'' . The curve is usually a semi-circular arc or a skewed arc. Franklin *et al.*³ suggested that for dilute solutions of polar substances in non polar solvents, the plot of the slopes α' vs α'' in the complex plane is similar to $\epsilon' - \epsilon''$ plot and can be used to

calculate the relaxation time. Higasi *et al.*⁴ have critically assessed the validity that the slopes α' and α'' can be used satisfactorily to calculate the relaxation time from the dilute solution studies. This idea led Higasi⁵ to formulate the equations to calculate the relaxation time at a single frequency. He concluded that slopes α' , α'' , etc., represent the polarizabilities ϵ' , ϵ'' , etc., and the earlier quantities can be directly taken in place of the later ones. Higasi *et al.*⁴ found that the Debye

equations for dilute solution can be represented by two independent equations indicating the group and molecular relaxation times of the solute molecule.

However, Scaife⁶ suggested that polarizability is a good measure of intrinsic properties of a substance and instead of ϵ' and ϵ'' , the real and imaginary part of polarizability (α^*) should be plotted to calculate the relaxation time; Chandra and Prakash⁷ have given a method to calculate the relaxation time from the polarizability plot for nearly spherical molecules. In this paper a new approach of calculating the relaxation time of non-rigid molecules using polarizability function plot has been proposed by plotting the real part of the polarizability function p' vs imaginary part p'' (where p' and p'' are calculated by using the slopes α' , α'' , etc.). The data⁸ on rigid polar molecules which behave as non-rigid molecules in the viscous medium has been taken to check the validity of the proposed equations. The relaxation times calculated using the proposed method are compared with the calculated values of relaxation times obtained using various methods^{4,5} and the literature⁸ values.

THEORY

When the dielectric constant becomes a complex quantity, the dielectric constant ϵ' and dielectric loss ϵ'' are given by the Debye equations

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + \omega^2\tau^2}, \quad (1)$$

$$\epsilon'' = \frac{\epsilon_0 - \epsilon_{\infty}}{1 + \omega^2\tau^2} \omega\tau. \quad (2)$$

The polarizability also becomes a complex polarizability $\alpha^*(\omega)$ and may be written as

$$\alpha^*(\omega) = \alpha' - i\alpha'' = \frac{\epsilon^* - 1}{\epsilon^* + 2}. \quad (3)$$

Cole-Cole¹ suggested that if ϵ' and ϵ'' are plotted, the plot is a semi circle and is given by

$$\epsilon^*(\omega) - \epsilon_{\infty} = \frac{\epsilon_0 - \epsilon_{\infty}}{1 + (i\omega\tau_c)^{1-\gamma}}, \quad 0 < \gamma < 1, \quad (4)$$

where γ is the distribution parameter and the relaxation time τ_c of the Cole-Cole method can be calculated with the following equation

$$\frac{v}{u} = (\omega\tau_c)^{1-\gamma}, \quad (5)$$

where v and u are the usual distances of the point on the semi circular arc.

According to Scaife, the complex polarizability may be written as

$$\alpha^* = \alpha_{(\infty)} + \frac{\alpha_{(0)} - \alpha_{(\infty)}}{1 + (i\omega\tau)}, \quad (6)$$

$$\alpha_{(\infty)} = \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2}, \quad (7)$$

$$\alpha_{(0)} = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \quad (8)$$

By substituting $\epsilon^* = \epsilon' - i\epsilon''$ in equation (3) the real part α' and imaginary part α'' of polarizability may be written as

$$\alpha' = \frac{\epsilon'^2 + \epsilon''^2 + \epsilon' - 2}{(\epsilon' + 2)^2 + \epsilon''^2}, \quad (9)$$

$$\alpha'' = \frac{3\epsilon''}{(\epsilon' + 2)^2 + \epsilon''^2}. \quad (10)$$

It has been found⁷ that the α' and α'' plot is identical to the Cole-Cole² plot and the relaxation time of approximately spherical molecules can be calculated from equation (11) and suggested that the frequency of dielectric data manifests itself as $(1 - \alpha_0 / 1 - \alpha_{\infty})\omega$.

$$\frac{v}{u} = \frac{1 - \alpha_0}{1 - \alpha_{\infty}} \omega\tau. \quad (11)$$

It has also been found⁷ that the polarizability plot represents the situation better than the $\alpha' - \alpha''$ plot obtained in the complex plane. Having no available method to calculate the relaxation time of flexible molecules from the polarizability plot, we propose here the modified expression of polarizability functions, replacing ϵ_0 , ϵ' and ϵ'' etc., in equations (7) to (10) by the corresponding slopes which may be defined as

$$p_{(0)} = \frac{a_0 - 1}{a_0 + 2}, \quad (12)$$

$$p' = \frac{a'^2 + a''^2 + a' - 2}{(a' + 2)^2 + a''^2}, \quad (13)$$

$$p'' = \frac{3a''}{(a' + 2)^2 + a''^2}, \quad (14)$$

$$p(\infty) = \frac{a_\infty - 1}{a_\infty + 1} \quad (15)$$

The quantities $p_{(0)}$, p' , p'' and $p_{(\infty)}$ have been calculated from the above equations. The plot of p' against p'' has been found to be a semicircle or a part of it. The relaxation time from these plots has been calculated using the following equation

$$v/u = (C\omega \tau_p)^{1-\gamma} \quad (16)$$

where $C = \frac{1-p_0}{1-p_\infty}$, v and u are the usual

distance and γ is the distribution parameter.

Here, p_0 and p_∞ are obtained from the polarizability function plot. Further equations (17) and (18) are proposed to calculate the relaxation time at a single frequency by using p' and p'' etc., defined earlier, corresponding to Higasi *et al.* equations. These equations have been used to calculate the relaxation time $\tau_p(1)$ associated with the group process and the relaxation time $\tau_p(2)$ representing the molecular process.

$$\tau_p(1) = \frac{1}{C\omega} \cdot \frac{p''}{p' - p_\infty} \quad (17)$$

$$\tau_p(2) = \frac{1}{C\omega} \cdot \frac{p_0 - p'}{p''} \quad (18)$$

The average relaxation time indicating the overall rotation $\tau_p(0)$ is the square root product of $\tau_p(1)$ and $\tau_p(2)$ and is calculated from the equation (19).

$$\tau_p(0) = [\tau_p(1) \cdot \tau_p(2)]^{\frac{1}{2}} \quad (19)$$

RESULTS AND DISCUSSION

The relaxation times τ_p , $\tau_p(1)$, $\tau_p(2)$ and $\tau_p(0)$ at the critical frequency have been calculated using equations (16), (17), (18) and (19), and are given in table 1. These values were compared with the corresponding values τ_{OH} , $\tau_{(1)}$, $\tau_{(2)}$ and $\tau_{(0)}$ calculated using the methods of Higasi and others^{4,5}.

d, l-camphor

The points are grouped on the high frequency side of the polarizability plot. The distribution parameter γ calculated at 20°C has been found to be 0.11 which agrees well with the value calculated by the Higasi method (0.11) and also with the literature⁸ value

(0.10). The relaxation time τ_p (14.0 ps) calculated using equation (16) is slightly low at 20°C but $\tau(0)$ (19.8 ps) and τ_{OH} (20.7 ps) are in good agreement. The $\tau_p(0)$ (25.8 ps) calculated by the proposed equation (19) is slightly higher than $\tau(0)$ and τ_{OH} . The relaxation times $\tau(1)$ (16.7 ps) and $\tau(2)$ (23.5 ps) are much closer to each other than the values $\tau_p(1)$ (16.2 ps) and $\tau_p(2)$ (41.3 ps). The wide separation in the values of $\tau_p(1)$ and $\tau_p(2)$ calculated with the proposed equations using p' , p'' , etc., is remarkable. This indicates that the relaxation corresponding to the two processes is much better resolved if suitably proposed equations (17) and (18) for the polarizability function are used instead of a' and a'' as proposed by Higasi *et al.*⁴.

Isoquinoline

The distribution parameter γ (0.25) calculated using the proposed method is not much different from the value of γ (0.30) calculated with the Cole-Cole¹ method, though the value (0.34) obtained using Higasi⁵ method is slightly higher. The relaxation time $\tau_p(0)$ (44.8 ps) is not much different from $\tau(0)$ (47.9 ps) and τ_{OH} (42.1 ps) and also from literature value⁸ τ_c (46.5 ps) at 20°C.

However, the separation of $\tau_p(1)$ (29.6 ps) and $\tau_p(2)$ (94.4 ps) is enhanced in case the suggested equations of polarizability are used instead of $\tau(1)$ and $\tau(2)$. This again points out the preference of using p' , p'' , etc., in place of a' , a'' , etc., used by Higasi *et al.*⁴ to have better resolution.

Acridine

The distribution parameter γ (0.4 and zero) calculated using the proposed method in nujol and decalin agrees well with the Cole-Cole plot. The relaxation time τ_p (211.3 ps) calculated from the polarizability plot at 40°C is slightly low in comparison to the literature value τ_c (230 ps) at 40°C. However, in decalin the values obtained using polarizability plot (= 34.4 ps) agrees well with τ_{OH} (= 33.0 ps) and the literature value⁸ τ_c (= 36.0 ps).

CONCLUSION

The relaxation times calculated using the proposed equations agree with the relaxation times calculated using various methods^{4,5} and the literature⁸ values. These results suggest that the frequency ω used in the analysis of dielectric data manifests itself as frequency factor ω^C [$C = (1 - p_0)/(1 - p_\infty)$], when the analysis of polarizability function data is made. It is further concluded that the resolution of relaxation time into its two components obtained using (17) and (18) seems to be better as compared to that obtained from the equation suggested by Higasi *et al.*⁴ as is evident from the widely separated values of $\tau_p(1)$ and $\tau_p(2)$ determined for all the three compounds studied.

TABLE I

Relaxation times calculated from polarizability function plots, equations (17), (18) and (19), Higasi method³, Higasi *et al.*¹ method and Cole-Cole² method

Compound	Temperature (°C)	Polarizability function plots		Using (17), (18), and (19)			Higasi method		Higasi <i>et al.</i> method			Cole-Cole method (lit) ⁸	
		τ_p ps	γ	$\tau_p(1)$ ps	$\tau_p(2)$ ps	$\tau_p(0)$ ps	τ_{OH} ps	γ	$\tau_{(1)}$ ps	$\tau_{(2)}$ ps	$\tau_{(0)}$ ps	τ_c ps	γ
d,l-Camphor Nujol	20	14.0	0.11	16.2	41.3	25.8	20.7	0.11	16.7	23.5	19.8	17.5	0.10
	40	9.5	0.11	13.9	21.0	17.1	14.3	0.09	12.8	17.2	14.8	12.8	0.10
	60	8.4	0.00	11.1	11.9	11.5	11.2	0.05	10.8	12.9	11.8	9.3	0.064
Isoquinoline Nujol	20	45.9	0.25	29.6	94.4	44.8	42.1	0.34	27.3	84.2	47.9	46.5	0.30
	40	27.0	0.20	19.1	51.5	31.4	38.0	0.26	16.8	40.8	26.2	25.1	0.21
	60	19.8	0.16	16.9	39.6	25.6	22.8	0.19	15.1	27.8	20.5	16.7	0.16
Acridine Nujol	20	1001.7	0.33	205.5	1223.3	501.4	1465	0.44	195.6	1118.0	467.6	1200	0.402
	40	211.3	0.20	129.4	373.3	219.7	226	0.36	128.7	424.0	233.6	230	0.308
	60	105.9	0.14	81.6	253.6	143.9	88.5	0.18	76.0	132.0	100.0	106	0.152
Acridine Decalin	20	55.0	0	60.3	52.3	56.2	—	0.045	62.0	60.6	61.0	55.5	0
	40	34.4	0	37.2	34.3	35.7	—	0.087	40.9	38.5	39.7	36.0	0
	60	25.9	0	22.4	23.3	22.8	23.6	0.16	23.6	27.0	25.2	25.7	0

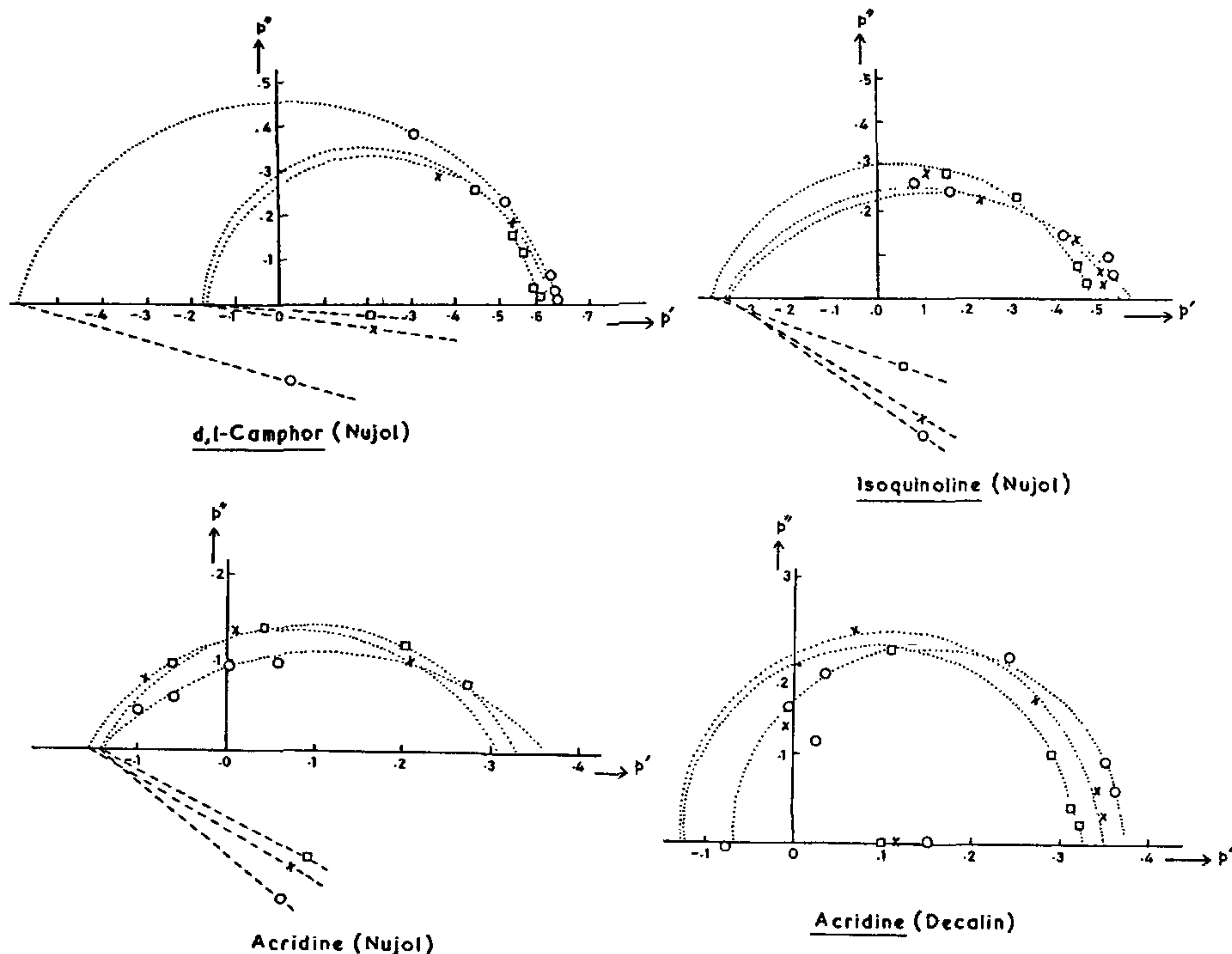


Figure 1.1. Arc plots of real part (p') and imaginary part (p'') of polarizability for the molecules under investigation; o, values at 20° C, x, values at 40° C, □, values at 60° C.

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