

CHAPTER IX

RADIO FREQUENCY CONDUCTIVITY AND RELAXATION TIME OF NITROBENZENE
IN BENZENE AND PARAFFIN SOLUTIONS

9.1 INTRODUCTION

The relation between dielectric relaxation time of dipolar molecule of polar liquid with its viscosity and size of the molecule has been studied by number of workers (Bottcher C.J.F. 1952). The measurement of relaxation time provides a means of investigating molecular motion and inter molecular action in liquid. In the Debye (1929) treatment the relaxation time τ of dipolar molecule was assumed to be due to the rotation of a sphere of radius a in a continuous viscous fluid whose internal viscosity is η and obtained an expression as $\tau = 4 \pi a^3 \eta / kT$. This expression has been applied with varying degree of success and failure using the value of directly measured macroscopic viscosity as internal viscosity.

Whiffen and Thompson (1946), Hall et al (1946), Cripwell and Sutherland (1946), Chaw, Le Fevre and Tardif (1957) showed that the Debye expression for dielectric loss ϵ'' due to microwave absorption by the solution of nitrobenzene in non-polar solvent C_6H_6 and CCl_4 , and in the mixed solvents of high viscous paraffin and CCl_4 , C_6H_6 , C_6H_{14} and CS_2 is fairly obeyed, but the Debye relation connecting relaxation time of polar molecule with macroscopic viscosity of the solution and radius of polar molecule does not hold good in these solutions. Jackson and Powles (1946) made a comparative study of the behavior of bromobenzene - benzene solution and bromobenzene - paraffin

solution and confirmed the inadequacy of the Debye relation of relaxation time τ with macroscopic viscosity η .

In continuation of the work described in the preceding chapter a further study has been made to know whether the Debye relation between τ and η is valid in the radio frequency electric field. In order to have a better idea of the above mentioned problem a comparative study has been done on the variation of r.f. conductivity K' and relaxation time τ at radio frequency electric field with the variation of viscosity η produced by changing temperature as well as by gradually adding high viscous paraffin solvent at room temperature.

9.2 RESULTS AND DISCUSSION

Experimental arrangement for the measurement of r.f. conductivity of polar liquid and its solutions in non-polar solvent at various concentration and temperatures has been given in Chapter VIII. Chemically pure nitrobenzene and benzene were used as solute and solvent respectively. Medicinal paraffin whose viscosity is 20 Cp and density is 0.81 gm/cc at 20°C was used as another non-polar solvent for making variable high viscous solution at a fixed temperature. The values of the viscosity η of nitrobenzene, paraffin and the mixed solutions were determined experimentally with the help of Oswald's viscometer. The values η of pure nitrobenzene have been compared with those given in International Critical Table.

In the previous chapter (Chapter VIII) the r.f. conductivity were measured for pure nitrobenzene at different temperatures and nitrobenzene in benzene at various concentrations and temperatures. In the present Chapter the values of r.f. conductivity of (i) nitrobenzene in liquid paraffin at different concentrations (ii) a fixed solution of 0.78 mole fraction of nitrobenzene in benzene at different temperatures and (iii) the fixed solution of nitrobenzene in benzene mixed with various percentage of solvent paraffin at room temperatures, have been measured. The values of r.f. conductivity K' , viscosity η ion density n calculated from the slopes of $K'-1/n$ curves, mobility ν and the relaxation time τ calculated from Ghosh and Chaudhury (1980) relation $\tau = \frac{2}{9} \frac{a e}{\nu k T}$ which is applicable for semi conducting organic polar liquid at r.f. field, are listed in Tables 9.1, 9.2 and 9.3.

The variations of r.f. conductivity K' of nitrobenzene as well as the fixed solution of 0.78 mole fraction of nitrobenzene in benzene with macroscopic viscosity η of the medium either by changing temperature or varying the proportion of liquid paraffin added to the system at 25°C are shown in Fig.9.1 and 9.2 respectively. Fig. 9.1 shows that the conductivity K' decreases exponentially with the increase of viscosity of the medium. This nature of variation of K' against η does not depend upon whether the change of η is due to the variation of temperature of the solution or by increasing the percentage of liquid paraffin in

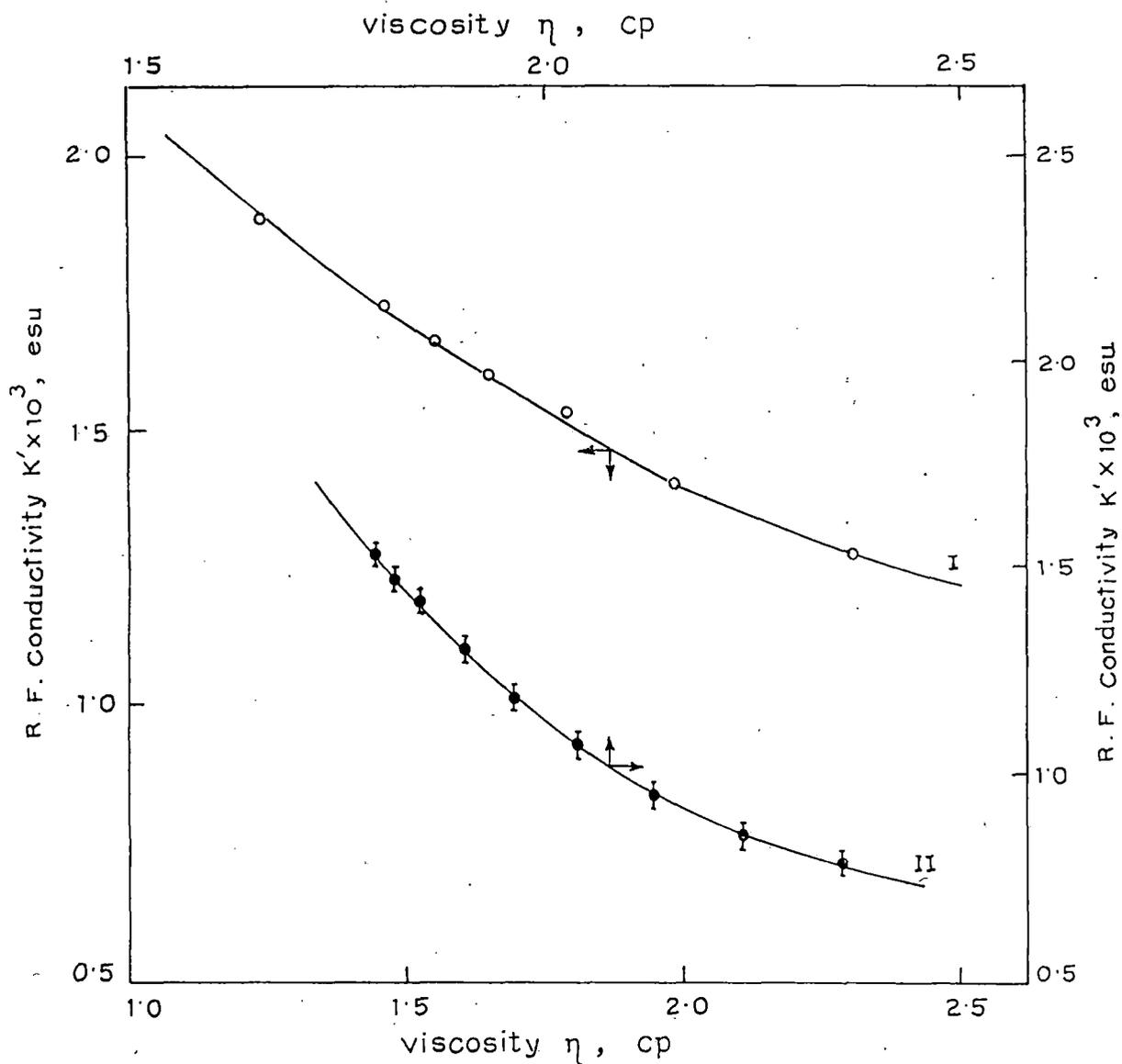


Fig. 9.1. Plot of $K' \times 10^{-3}$ vs viscosity (η) of
 I (—○—) Nitrobenzene at different temperatures
 II (—●—) Nitrobenzene + Paraffin mix at 25°C

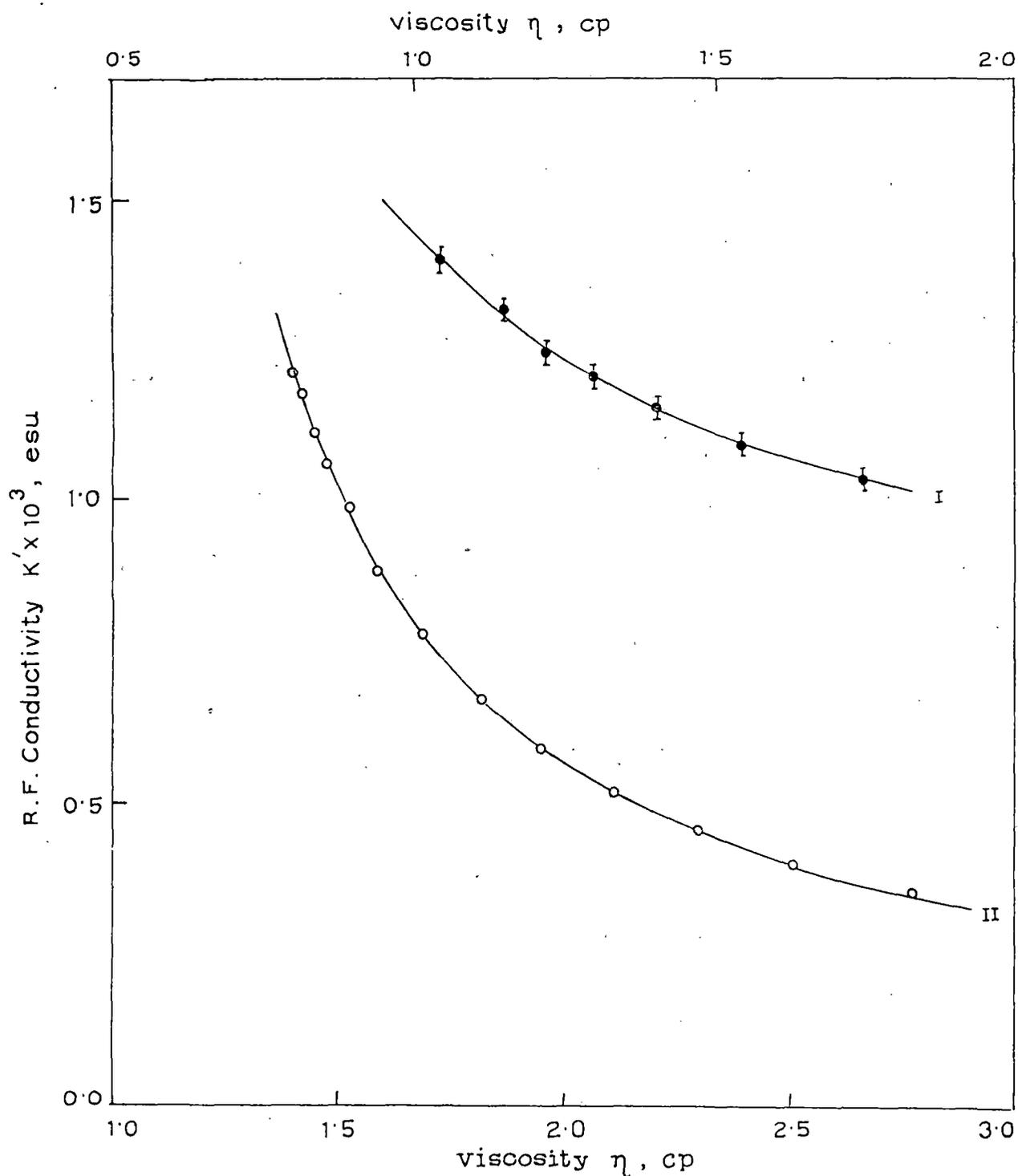


Fig. 9.2. Plot of $K' \times 10^3$ vs viscosity η
 I (—●—) a fixed solution of 0.78 mole fraction of nitrobenzene
 in benzene at various temperatures.
 II (—○—) the fixed solution + Paraffin at 25°C

Table 9.1 - Values of viscosity η , ion density n , r.f. conductivity mobility ν , relaxation time τ ,

$\gamma = \Delta H\tau/\Delta H\eta$, and radius a of nitrobenzene in nitrobenzene plus paraffin mixture at 25°C

% of Paraffin	η CP	$n \times 10^{-12}$	$K \times 10^{-9}$ esu	$\nu \times 10^4$ cm ² /volt/sec	$\tau \times 10^{11}$ sec	γ From Graph	$\frac{\tau}{\eta} \times 10^9$	$\frac{\tau}{\eta^\gamma} \times 10^9$	$a^{\circ A}$ with $\eta_{int} = \eta$	$a^{\circ A}$ with $\eta_{int} = \eta^\gamma$
0.0	1.79	34.9	1.5280	3.0343	4.91		2.74	9.51	2.08	3.15
0.9	1.82	34.3	1.4700	2.9762	5.02		2.76	9.57	2.08	3.15
2.0	1.85	33.4	1.4205	2.9535	5.05		2.73	9.41	2.08	3.13
3.7	1.90	31.9	1.2953	2.8198	5.29		2.78	9.49	2.09	3.14
5.5	1.97	30.5	1.1761	2.6761	5.56	1.31	2.83	9.56	2.10	3.15
7.5	2.04	28.9	1.0640	2.5549	5.84		2.87	9.58	2.11	3.15
9.8	2.13	27.1	0.9484	2.4285	6.15		2.89	9.52	2.11	3.15
12.3	2.24	25.2	0.8502	2.3429	6.37		2.85	9.25	2.10	3.12
14.0	2.35	23.9	0.7844	2.2792	6.55		2.78	8.87	2.09	3.07

Table 9.2 - Values of viscosity η , ion density n , r.f. conductivity K' , mobility v , relaxation time τ ,

$\gamma = \Delta H\tau/\Delta H\eta$, and radius a of nitrobenzene in a fixed solution (0.78 mole fraction of nitrobenzene in benzene) plus paraffin mixture at 25°C

% of Paraffin	η CP	$n \times 10^{-12}$	$K' \times 10^{-9}$ esu	$v \times 10^4$ cm ² /volt/sec	$\tau \times 10^{11}$ sec	γ From Graph	$\frac{\tau}{\eta} \times 10^9$	$\frac{\tau}{\eta\gamma} \times 10^9$	a °A with $\eta_{int} = \eta$	a °A with $\eta_{int} = \eta\gamma$
0.00	1.40	18.9	1.2100	4.4412	3.36		2.40	9.37	1.99	1.45
0.72	1.43	18.6	1.1709	4.3669	3.42		2.40	9.42	1.99	1.46
1.71	1.45	18.2	1.1069	4.2328	3.53		2.44	9.61	2.00	1.47
3.20	1.48	17.6	1.0576	4.1635	3.59		2.43	9.61	2.00	1.47
5.20	1.52	16.8	0.9824	4.0608	3.68		2.42	9.62	1.99	1.47
8.00	1.59	15.7	0.8790	3.8979	3.83		2.41	9.70	1.99	1.47
11.50	1.69	14.4	0.7759	3.7418	3.99	0.78	2.37	9.64	1.98	1.47
15.85	1.81	13.0	0.6714	3.5976	4.15		2.29	9.48	1.96	1.46
19.77	1.95	11.8	0.5927	3.4881	4.28		2.20	9.24	1.93	1.45
23.76	2.11	10.6	0.5187	3.3854	4.41		2.09	8.96	1.90	1.43
27.75	2.30	9.5	0.4528	3.3030	4.52		1.96	8.57	1.86	1.41
31.68	2.51	8.6	0.4010	3.2456	4.60		1.83	8.14	1.82	1.39
35.20	2.77	7.6	0.3525	3.2041	4.66		1.68	7.63	1.77	1.36

Table 9.3 - Values of viscosity η , r.f. conductivity, K' , mobility ν , relaxation timer ,

$\gamma = \Delta H\tau/\Delta H\eta$, and radius of nitrobenzene in a fixed solution of 0.78 mole fraction

of nitrobenzene in benzene at different temperatures.

t °C	η CP	$K \times 10^{-9}$ esu	$\nu \times 10^4$ cm ² /volt/sec	$\tau \times 10^{11}$ sec	γ From Activa- tion energy	γ From Graph	$\frac{\tau T}{\eta} \times 10^7$	$\frac{\tau T}{\eta \gamma} \times 10^7$ with $\gamma = 0.78$	a ^o A with $\eta_{int} = \eta$	a ^o A with $\eta_{int} = \eta \gamma$
15	1.75	1.0354	3.8004	3.93			6.4588	2.6531	1.92	1.43
20	1.54	1.0901	4.0011	3.79			7.2010	2.8759	1.99	1.47
25	1.40	1.1527	4.2309	3.53			7.4989	2.9332	2.02	1.48
30	1.30	1.2094	4.4390	3.31	0.53	0.78	7.7393	2.9748	2.04	1.48
35	1.22	1.2472	4.5778	3.16			7.9941	3.0309	2.06	1.49
40	1.15	1.3146	4.8251	2.95			8.0648	3.0087	2.07	1.49
50	1.04	1.0380	5.1169	2.69			8.3706	3.0642	2.09	1.50

the solution at a fixed temperature. Similar results have been obtained in case of the fixed solution of nitrobenzene in benzene (Fig 9.2).

It has been suggested (Smyth 1955) that when the polar molecules are surrounded by non-polar ones, the relaxation time τ is influenced by the nature of non-polar molecules as well as by the viscosity of the solution as a whole. If the shape of the molecule, undergoing dipole orientation, depart little from that of a sphere, it can rotate without any considerable displacement of the surrounding molecules. In this case the relaxation time is relatively insensitive to the macroscopic viscosity of the solution, which is obtained with the help of usual Laboratory method. But if the molecule is not spherical in shape, its rotation must involve the displacement of the neighboring molecules and corresponding τ should depend markedly upon the viscosity of the solution as well as upon the molecular size. Nitrobenzene is a non-spherical molecule. So it is of great interest to ascertain whether the relaxation time τ of nitrobenzene molecule in low viscous benzene solvent and in high viscous paraffin solvent are related in an analogous manner to the macroscopic viscosity η of the solution. A desired comparative statements of the results are given in Table 9.4. It indicates that the relation taken from Debye expression:

Table 9.4 - Comparison of relaxation time and macroscopic viscosity of nitrobenzene at 25°C

Solvent	Viscosity η CP	Relaxation time $\tau \times 10^{11}$ Sec.	Viscosity Ratio $\frac{\eta_{\text{para}}}{\eta_{\text{Ben}}}$	Relaxation time ratio $\frac{\tau_{\text{para}}}{\tau_{\text{Ben}}}$
Benzene	0.70	1.30		
Paraffin	2.36	6.55	3.4	5.0

$$\frac{\tau_{NB + Prfn}}{\tau_{NB + Bnzn}} = \frac{\eta_{NB + Prfn}}{\eta_{NB + Bnzn}} \dots\dots\dots(9.1)$$

is not valid. Thus τ is far from being proportional to η originally suggested by Debye equation: $\tau = 4 \pi a^3 \eta / kT$, a being the molecular radius.

Fig. 9.3 shows the variation of τ with the % of benzene in nitrobenzene as well as with the % of paraffin in nitrobenzene and the fixed solution. As the % of paraffin increases the τ value increases given convex nature in both the solutions. But in benzene solution τ of nitrobenzene increases in a concave manner with the decrease of % of benzene. The variations of relaxation time τ of nitrobenzene of the fixed solution against macroscopic viscosity η by changing temperature as well as by gradually adding paraffin liquid are shown in Fig.9.4. The figure shows that the τ increases linearly as the viscosity η increases upto a particular value of macroscopic viscosity η_{c1} and then increases but markedly deviates from from the linearity. The value of the critical macroscopic viscosity after which $\tau \propto \eta$ does not hold good has been found from the graphs (Fig 7.4), to be $\eta_{c1} = 1.52$ cp. It suggests that the Debye equation is inapplicable to the cases where the viscosity of the solution is greater than of about 1.52 cp.

Jackson and Powles (1946) determined the relaxation time τ of benzophenone in benzene and paraffin at 19°C and observed that

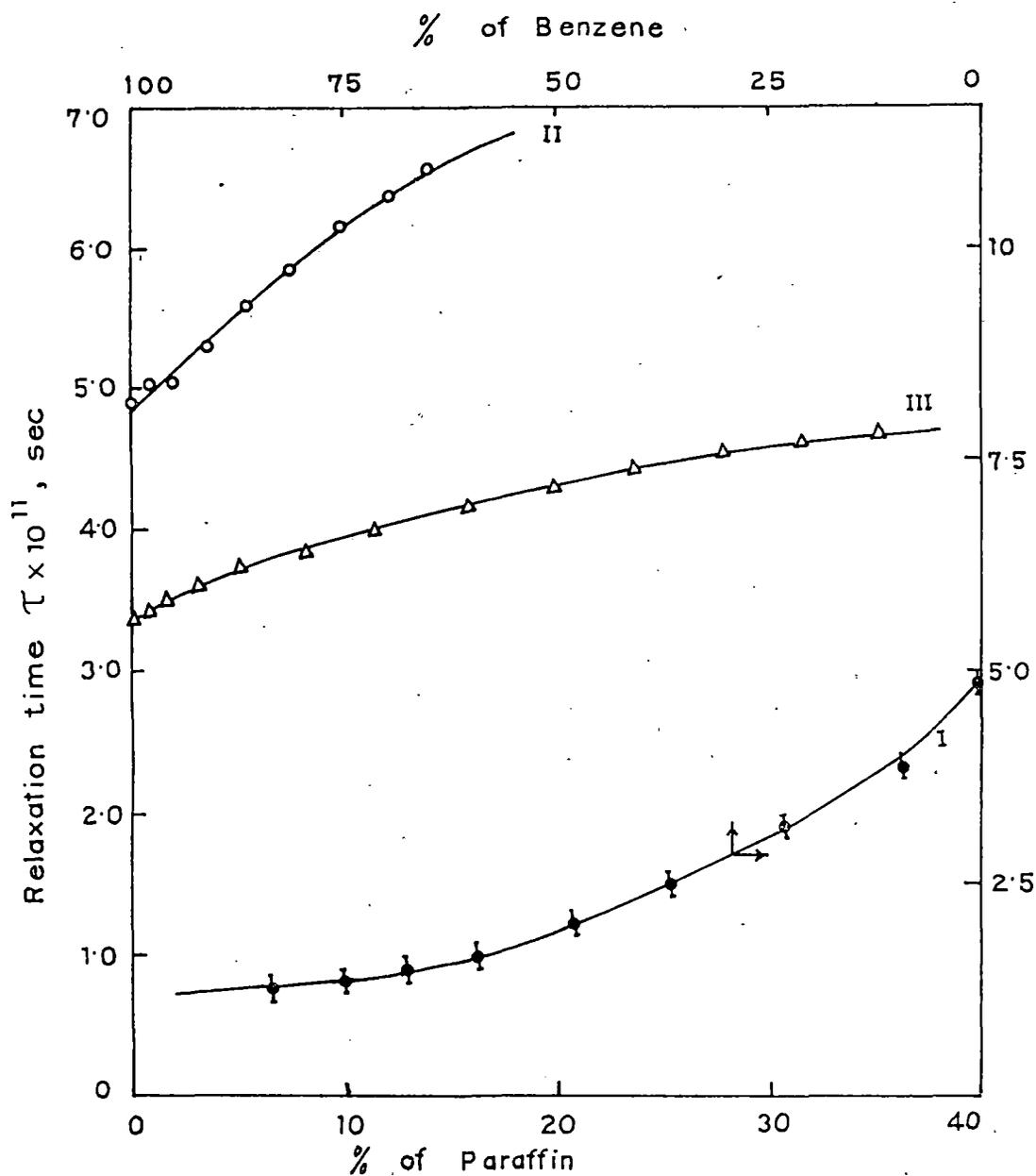


Fig. 9.3. Variation of relaxation time τ against % of benzene or paraffin.
 I (—●—) nitrobenzene + benzene at 25°C
 II (—○—) nitrobenzene + paraffin at 25°C
 III (—△—) [0.78 mole fraction of nitrobenzene in benzene] + paraffin at 25°C.

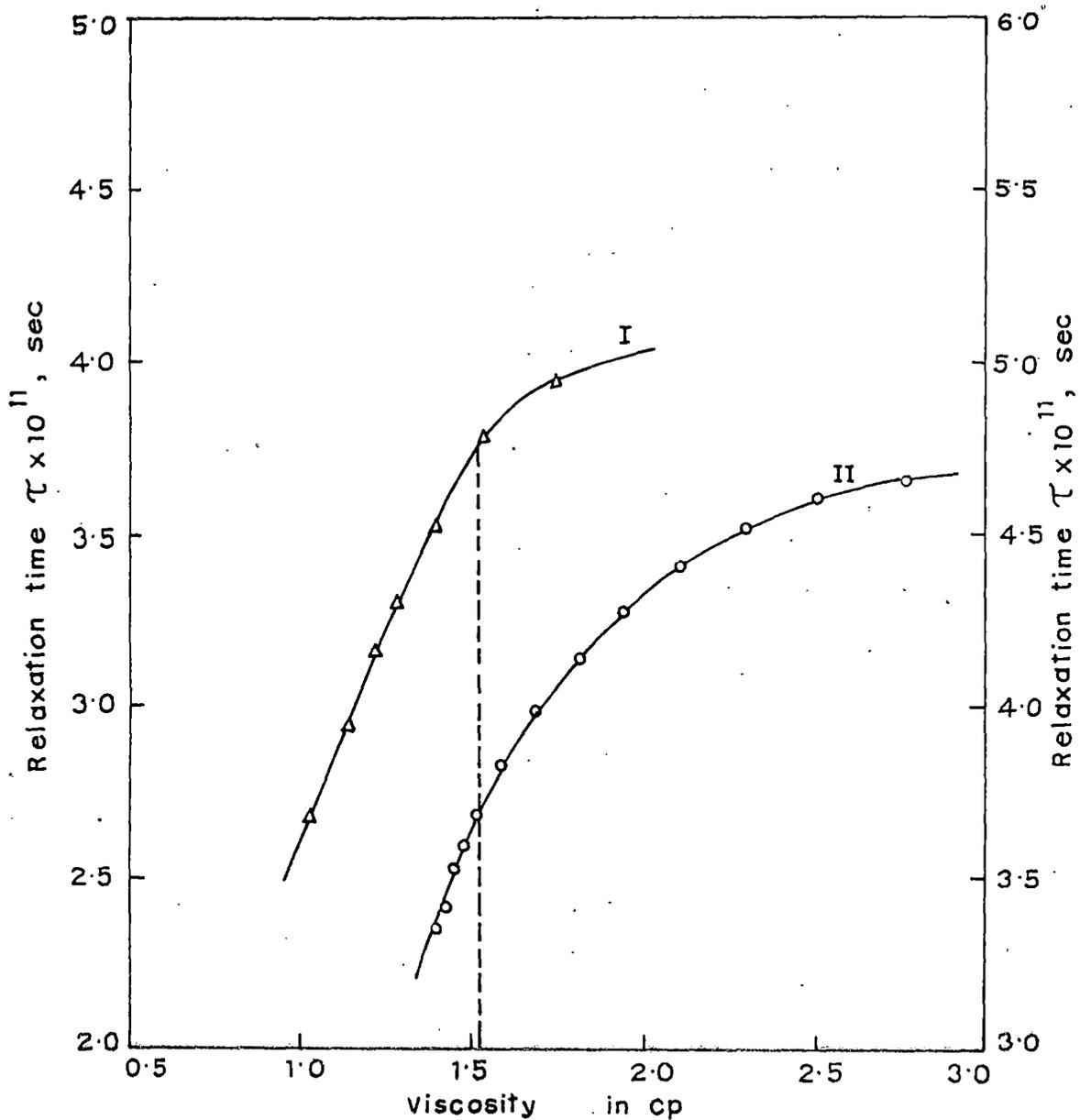


Fig. 9.4. Plot of relaxation time τ against viscosity η

I (— Δ —) a fixed solution of 0.78 mole fraction of nitrobenzene in benzene at various temperatures

II (— \circ —) the fixed solution + paraffin at 25°C

the τ in paraffin appears to be 18 times that in benzene solution when the ratio of viscosities of paraffin and benzene is 2.98 at this temperature. A systematic examination of the influence of different solvents on the relaxation time τ of nitrobenzene was made by Whiffen (1950) and the results are given in Table 9.5. It is observed from Table 9.5 that the τ for nitrobenzene are not closely parallel to the viscosity of the solvents as given by Debye formula. Higasi (1961) emphasized that not only the solute molecules will slip in rotation past the solvent molecules, but also showed that the intermolecular interactions exceeding KT in energy may cause appreciable sticking of molecules. He observed that the ratio of the relaxation time of a polar molecule in two non-polar solvents CCl_4 and C_6H_{12} whose viscosity differs not more than 1% becomes $\tau_{CCl_4} / \tau_{C_6H_{12}} = 1.8 \pm 0.3$ and suggested an expression $\tau = \text{const. } \eta^\gamma$ where $\gamma = \Delta H_\tau / \Delta H_\eta$.

The variation of τ and η with temperature can be expressed in terms of following equations (Whiffen and Thompson 1946)

$$\tau = A \exp (\Delta H_\tau / RT) \quad \dots\dots\dots (9.2)$$

$$\eta = B \exp (\Delta H_\eta / RT) \quad \dots\dots\dots (9.3)$$

Where A and B are approximately constant over the temperature range of the present experiment and ΔH_τ and ΔH_η are the enthalpies of activation for dielectric relaxation and viscous flow respectively.

Table 9.5 - Relaxation time of nitrobenzene in different solvents

according to the measurements of Whiffen (1950) at 20°C

Solvent	Viscosity η CP	Relaxation time $\tau \times 10^{11}$ Sec	$\frac{\tau}{\eta} \times 10^9$
Carbon disulphide	0.37	0.86	2.32
n - Heptane	0.42	0.68	1.62
Benzene	0.65	1.28	1.97
Cyclohexane	0.97	0.95	0.98
Carbon-tetra- chloride	0.97	1.52	1.57

From eqn (9.2) and (9.3) we get

$$\tau/\eta = (A/B) \exp (\Delta H\tau - \Delta H\eta) / RT \quad \dots\dots\dots(9.4)$$

Taking $\Delta H\tau = \eta \Delta H\eta$ we have from eq (9.4)

$$\begin{aligned} \tau &= (AB^{-\gamma}) \eta^{\gamma} \\ \tau &= \text{const. } \eta^{\gamma} \quad \dots\dots\dots(9.5) \end{aligned}$$

This equation (9.5) indicates the relaxation time is a simple function of η^{γ} . Therefore the plot of $\log \tau$ against $\log \eta$ should be a straight line. Fig. 9.5 and 9.6 represents the plot of $\log \tau$ versus $\log \eta$ for nitrobenzene + paraffin mixtures and the fixed solution (0.78 mole fraction of nitrobenzene in benzene) + paraffin mixtures at 25°C. These figures show that the curves are straight line, but at the higher viscosity region the linearity does not hold. The critical viscosity η_{c2} upto which the linearity $\tau \propto \eta^{\gamma}$ holds good has been found to be 1.93 cp and 2.1 cp from the Figs 9.5 and 9.6 respectively. Again the values of τ/η and τ/η^{γ} indicates the same results (Table 9.1 to 9.3).

Even allowing the free space between packed molecules the value of the molecular radius 'a' calculated from the density of nitrobenzene is 3.4°A, which is much higher than the values obtained from Debye relation $\tau = 4\pi a^3 \eta / kT$ using η_{int} is equal to macroscopic viscosity η and η^{γ} as shown in Table 9.1 to 9.3. The calculated values of radius 'a' using $\eta_{int} = \eta$ are found to be

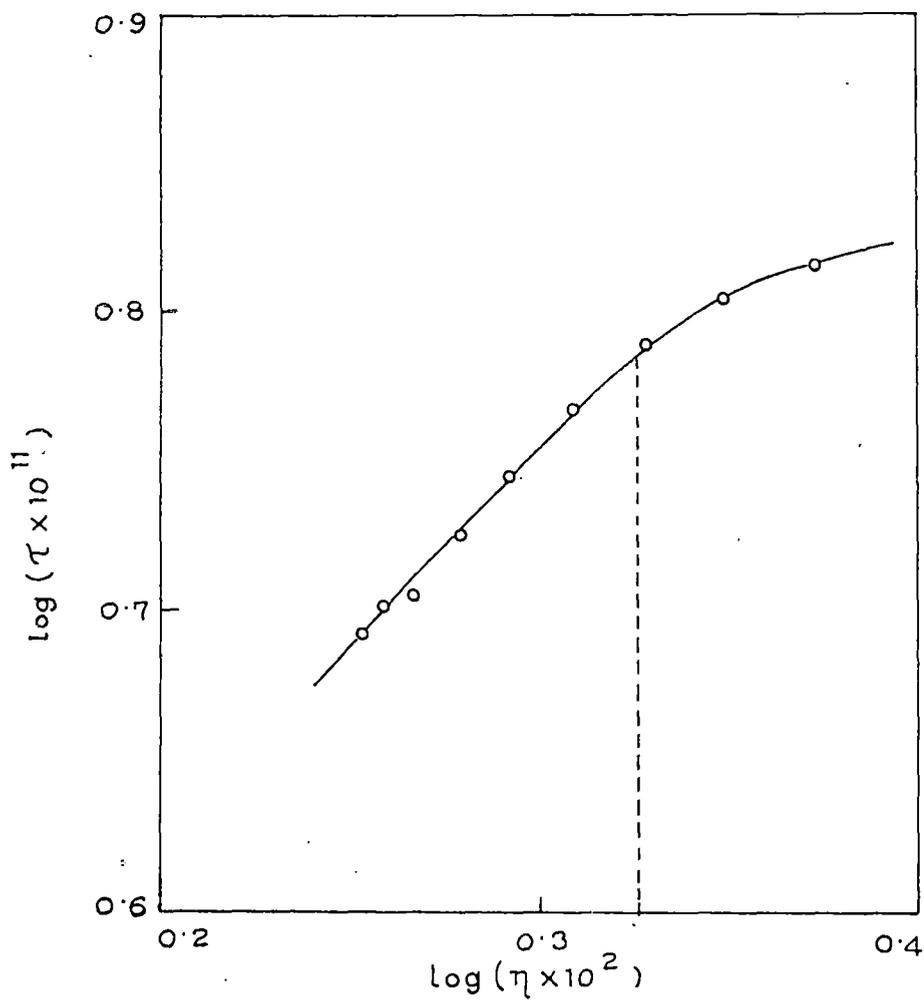


Fig. 9.5. Plot of $\log(\tau \times 10^{11})$ vs $\log(\eta \times 10^2)$ of nitrobenzene + paraffin at 25°C.

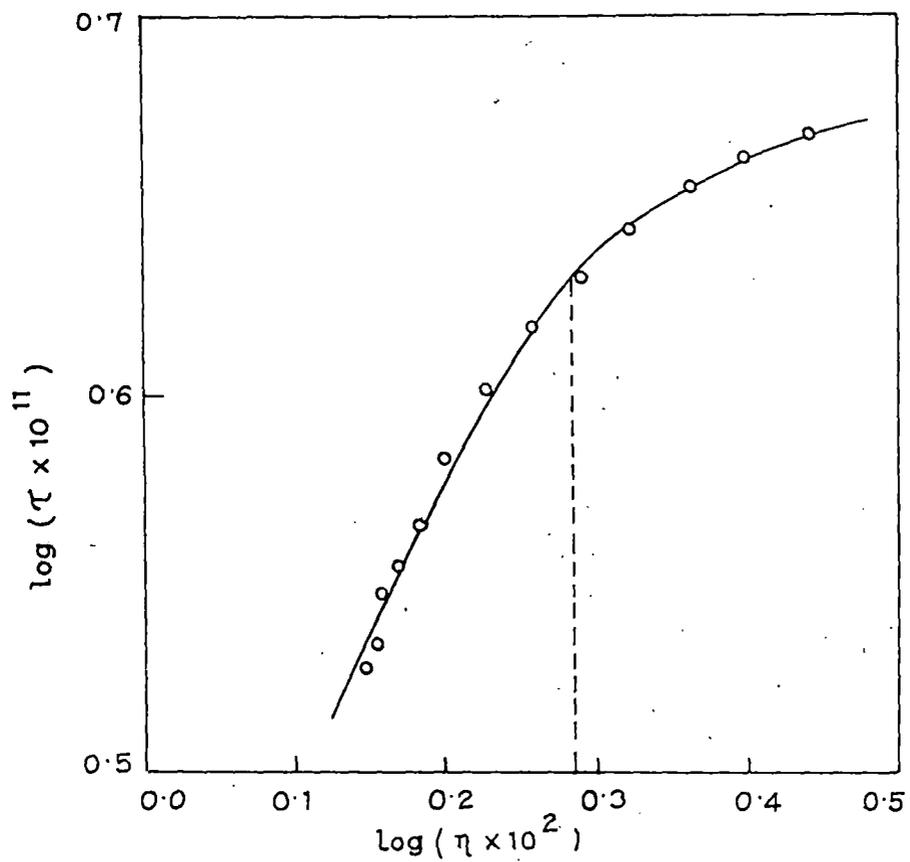


Fig. 9.6. Plot of $\log(\tau \times 10^{11})$ vs $\log(\eta \times 10^2)$ of (0.78 mole fraction of nitrobenzene in benzene) + paraffin at 25°C.

nearly constant upto $\eta \approx 1.5$ cp, but the 'a' values calculated using $\eta_{int} = \eta^x$ are fairly constant upto η is about 2cp.

Therefore it may be suggested that the relaxation time τ is far from being proportional to the macroscopic viscosity η . So it may be assumed that the Debye equation is inadequate in describing the relation between τ and η . This discrepancy probably arises from the experimental facts that the macroscopic viscosity η is used in place of internal viscosity η_{int} . Thus the assumption $\eta_{int} = \eta$ is inapplicable in representing the variation of relaxation time of a polar molecule with the viscosity of the medium also in the radio frequency electric field.

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