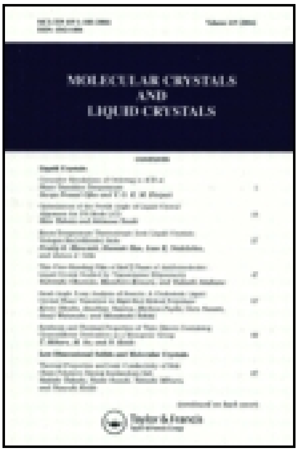

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# Dielectric Studies for Dipole-Dipole Association of Mesogenic Molecules in Para-Xylene

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# DIELECTRIC STUDIES FOR DIPOLE-DIPOLE ASSOCIATION OF MESOGENIC MOLECULES IN PARA-XYLENE

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ABSTRACT Results are reported for dipole-dipole association of mesogenic molecules in para-xylene solution. Measurements of Kirkwood correlation factors for solutions of 4-n-pentyl-4-cyanophenyl cyclohexane (PCH5) and 4-n-heptyl-4-cyanophenyl cyclohexane (PCH7) are interpreted in terms of new model by Dunmur et al.[10] for dipole-association. Results suggest that the molecular association depends on molecular shape and polarizability anisotropy of the system.

## INTRODUCTION

Dipole-Dipole interaction occurs in systems containing molecules with permanent dipole moment. Though these interactions are not mainly responsible for the formation and stability of mesophase, but important in determining some of the physical properties of liquid crystals. The dielectric properties of liquid crystals with strongly polar end group such as cyano- or nitro- have been interpreted in terms of anti-parallel molecular association.[1,2] The reentrant nematic phenomena[3,4] and discontinuous jump in average dielectric permittivity ($\bar{\epsilon}$) near the nematic—isotropic transition in strongly polar liquid crystals can be attributed by the existence of anti-parallel dipole correlation.[5] The lowering of dipole moment of strongly polar liquid crystal compounds in the nematic phase of cyanobiphenyls is attributed due to anti-parallel dipole-dipole association.[6,7]

The effect of such antiparallel ordering in some nematic mixtures is to increase the ratio of the bend and splay elastic constants.[5] X-ray measurements also suggests that layer spacing is greater than molecular length and which has been attributed antiparallel association due to dipole-dipole and dipole-induced dipole interactions.[8,9] By studying the properties of mesogenic molecules in solution at different concentrations, it is possible to obtain an idea of some physical behaviour of mesogenic molecules.[10,11] A few number of studies have been done on dipolar association of mesogenic molecules in solutions and a new model has been proposed,[10] which can explain the dielectric behaviour of polar nematic liquid crystals in terms of antiparallel and parallel association in different proportions. Dunmur and Toriyama[16] have already reported the quantitative studies of the molecular associations on CB5 and CCH5 in isotropic solvent. Apart from cyano-group, one molecule (CB5) possesses two highly polarizable phenyl groups due to de-localised $\pi$-electron; whereas the other molecule is completely lacking of $\pi$-electron in the core. In our case we have taken two liquid crystalline compounds (PCH5 and PCH7) both of which have one phenyl group and one cyclohexyl group in the core. In the present paper, dielectric studies have been made in PCH group (PCH5,PCH7) of mesogenic molecules in para-xylene solution in different concentrations. The results are discussed in terms of Kirkwood correlation factor $g_1$ and on the proposed model by Dunmur et al.[10]

## THEORETICAL BACKGROUND AND EXPERIMENTAL PROCEDURE

The dipole correlation function over a macroscopic volume gives the Kirkwood correlation factor $g_1$. The $g_1$ for polar solute in nonpolar solvent may be obtained from the measurement of the effective dipole moment ($\mu_{eff}$). The effective dipole moment is less than that of free molecule dipole moment ($\mu_m$) such that $g_1 = \mu_{eff}^2 / \mu_m^2$. The $g_1$ values at different concentrations were measured using the following relation[12]

$$g_1 = \frac{9kT\epsilon_o(2\epsilon + n_2^2)^2}{\mu^2 N_A X_2 (n_2^2 + 2)^2 \ (2\epsilon + 1)} \left\{ \frac{\epsilon - 1}{\epsilon} \left[ \frac{X_1M_1 + X_2M_2}{d} \right] - \frac{3\ X_1M_1(\epsilon_1 - 1)}{d_1(2\epsilon + \epsilon_1)} - \frac{3\ X_2M_2(n_2^2 - 1)}{d_2\ (2\epsilon + n_2^2)} \right\} \qquad (1),$$

where $\epsilon_o$ is the permittivity of free space; $\epsilon$, n and d are the permittivity, refractive index and density of solution. $\epsilon_1$ and $d_1$ refer to the pure solvent, $X_2$ is the mole fraction of solute, $X_1$ is the mole fraction of solvent and $M_1$ and $M_2$ are the molecular weights of the solvent and solute molecules respectively. $\mu$ is the dipole moment of free molecule is obtained by extrapolation to low concentration where $g_1 = 1$. Dunmur et al[10] introduced a model for molecular association which was used to explain the dielectric properties of mesogenic solution. The proposed model based on the assumption that both parallel and anti-parallel correlation of the molecular axes may occur in mesogenic solution and in actual calculation they had restricted the attention only to dimer formation and higher aggregates had been neglected. The dynamic equilibrium between the single molecule and associated pairs exists and is described by the mass- action equations

$$2M \rightleftharpoons M_{2a}, \quad 2M \rightleftharpoons M_{2p}$$

with equilibrium constants $K_a$ and $K_p$ for antiparallel and parallel dimers respectively and the $K_a$, $K_p$ can be related to mole fraction of monomer ($X_m$) and parallel ($X_p$) and antiparallel ($X_a$) dimers as $K_a = X_a / X_m^2$, $K_p = X_p / X_m^2$.

The $X_m$ is related to $X_2$, $X_a$ and $X_p$ by the relation[10]

$$X_m = \frac{\left[1 + 4X_2(2 - X_2)(K_a + K_p)\right]^{1/2} - 1}{2(2-X_2)(K_a+K_p)} \quad (2),$$

Again for a solution containing $N_k$ associated species for which the multimer dipole moment is $\mu_k$, then the correlation factor $(g_1)$ is given by[13]

$$g_1 = \frac{1}{\mu_m^2} \sum N_k \mu_k^2 / \sum N_k \quad (3),$$

considering only parallel and antiparallel dimers

$$g_1 = \frac{1}{X_2(1 + X_a + X_p)} \left\{ X_m + X_p(\mu_p/\mu_m)^2 + X_a(\mu_a/\mu_m)^2 \right\} \quad (4),$$

where $X_m$, $X_p$ and $X_a$ are mole fractions of the monomer, parallel and antiparallel dimers respectively. In Figure 1, the curves showing the dependence of dielectric permittivity with concentration of PCH molecules in para-xylene. Dipole correlation factor $g_1$ for 4-n-pentyl-4-cyanophenyl cyclohexane ( PCH5 ) and 4-n-heptyl-4-cyanophenyl cyclohexane ( PCH7 ) has been calculated from the measurement of dielectric permittivity, refractive index and density in para-xylene solution using equation (1). The measurements were carried out at (25 ± 0.5) °C. The dielectric permittivity was measured in a ITO coated glass with 60 μm mylar spacer by using a GRE bridge. The refractive index was measured with Abbe Refractometer.

## RESULTS AND DISCUSSION

The calculated dipole moments of PCH molecules in the present studies - as shown in Table 1 - are consistent with those reported values of PCH5[15] and PCH7[14]. The $g_1$ values for PCH5 and PCH7 in para-xylene (Fig.2) are almost the same at whole range of concentration indicating that the association in these molecules develops in similar way. The $g_1$ values in both the cases are less than 1.00 indicating association in these molecules develops in similar way. The $g_1$ values in both the cases are less than 1.00 indicating that antiparallel association dominates in both cases which is generally observed in all polar molecules when the dipole direction is along the long axis of the molecules[2]. For comparison the $g_1$ values of PCH materials in the present study and the $g_1$ values obtained from the previous studies[16] for CB-5 and CCH-5 liquid crystals are also included in Fig. 2 as a function of solute mole fraction

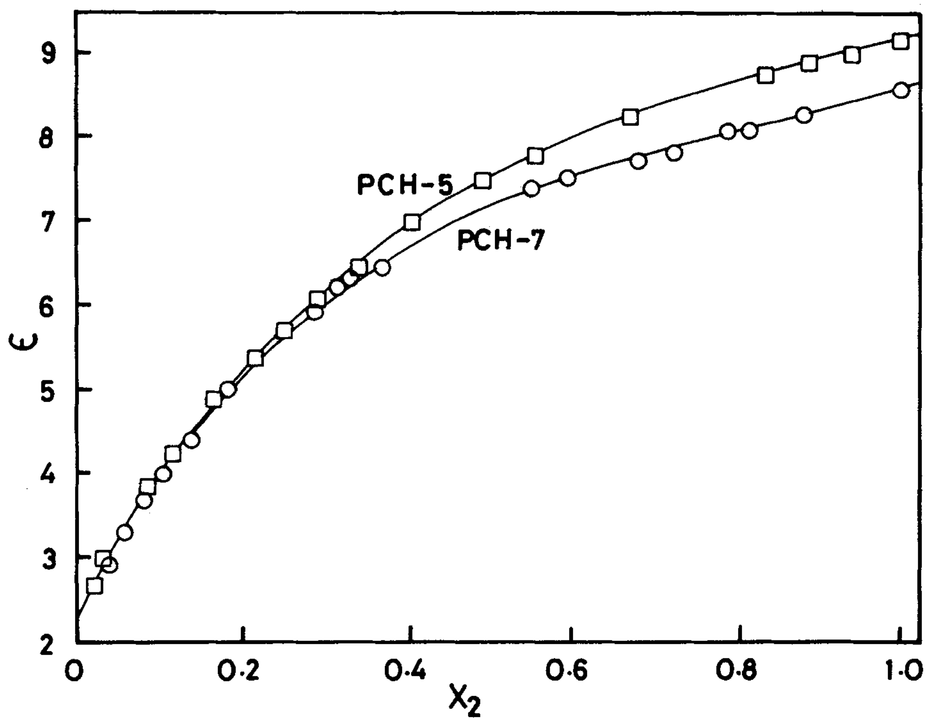

FIGURE 1 Dielectric Constant (ε) as a function of mole fraction ($X_2$) for para-xylene solutions of mesogens at 25°C.

TABLE I Dipole moment ($\mu$) and association constants ($K_a$,$K_p$) of PCH5 and PCH7.

| | PCH5 | PCH7 |
|---|---|---|
| Dipole Moment $\mu$ (Debye) | 4.31 | 4.47 |
| Association Constant Antiparallel $K_a$ | 0.96 ± 0.07 | 1.76 ± 0.03 |
| Association Constant Parallel $K_p$ | 0.14 ± 0.05 | 0.22 ± 0.03 |

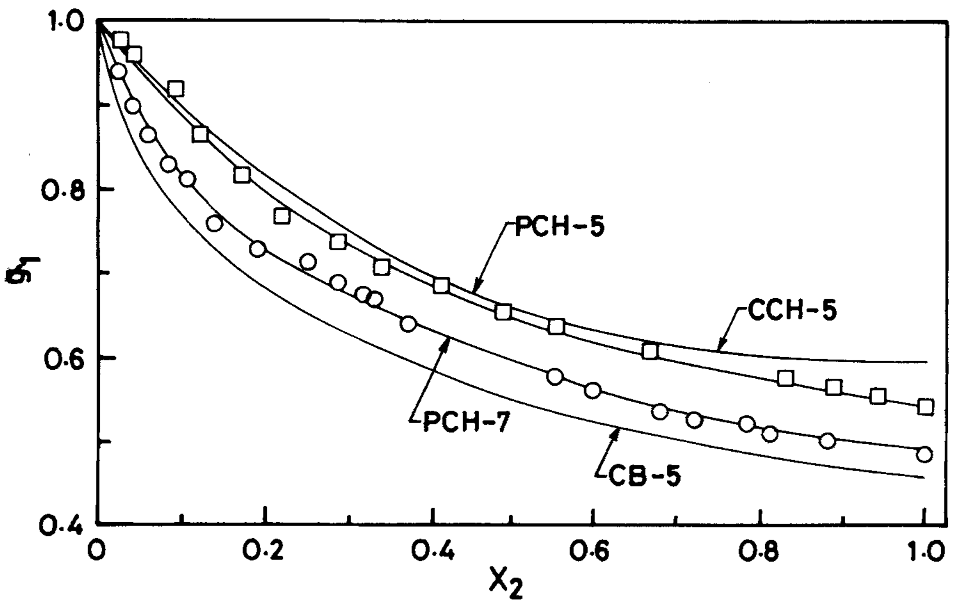

FIGURE 2 Dipole correlation factors ($g_1$) of PCH5, PCH7, CB5 and CCH5[16] as a function of mole fraction ($X_2$) for para-xylene solutions of mesogens at 25°C.

($X_2$) in para-xylene solution over all concentration range at 25°C.

It is shown in Fig.2 that the $g_1$ values of PCH group lies in between the $g_1$ values of CB-5 and CCH-5, which predicts that the degree of association is the highest in CB-5 molecules ,but both PCH molecules have greater degree of association than that of CCH-5 molecules, which is quite obvious from the fact that the degree of conjugation is different due to the different molecular structure of these compounds, though all the compounds have strongly polar cyano group. The cyanobiphenyls has higher polarizability anisotropy than those of PCH and CCH molecules[15]. So the $g_1$ values of the molecules may be correlated with polarizability anisotropy of these molecules. The extrapolated $g_1$ values of PCH-7 at higher concentrations (when solute mole fraction = 1) is around 0.5 and it is comparable to the $g_1$ values obtained for PCH7 at isotropic phase by Schadt et al.[2] The $g_1$ values (Fig.2) of PCH-5, PCH-7 indicate that the association develops in both the molecules in the same manner but a little smaller $g_1$ value in PCH7 may be explained due to a little higher polarizability anisotropy[17] of PCH7 due to elongated structure of the latter. In order to calculate the equilibrium constants $K_a$ and $K_p$ the necessary assumptions were made to set dipole moment $\mu_p = 2\mu_m$ and $\mu_a = 0$, in the present case where the molecules have taken as cylindrically symmetric and the dipole moment is along the cylinder axis.

The equilibrium constants $K_a$ and $K_p$ have been determined after knowing the experimental values of $g_1$ from equation (1) and fitting these values in equations (4) and (2). Our results for $K_a$ and $K_p$ in PCH molecules (given in Table I) and those obtained in CB-5 and CCH-5[16] suggest that the degree of association are consistent with polarizability anisotropy of these molecules. Also if we compare the degree of association of PCH-5 and PCH-7, a little larger ($K_a + K_p$) value of PCH-7 than that of PCH-5 is consistent with larger polarizability anisotropy due to extended shape of PCH-7. The ratio of $K_a$ / $K_p$ value is almost the same for PCH-5 and PCH-7 and this value is around 8:1 which indicates that there are about eight times antiparallel dimers than parallel dimers. The monomer, parallel and anti-parallel dimer concentrations as determined from the measured values of dielectric constant with the help of equation (2) is shown in Figure 3.

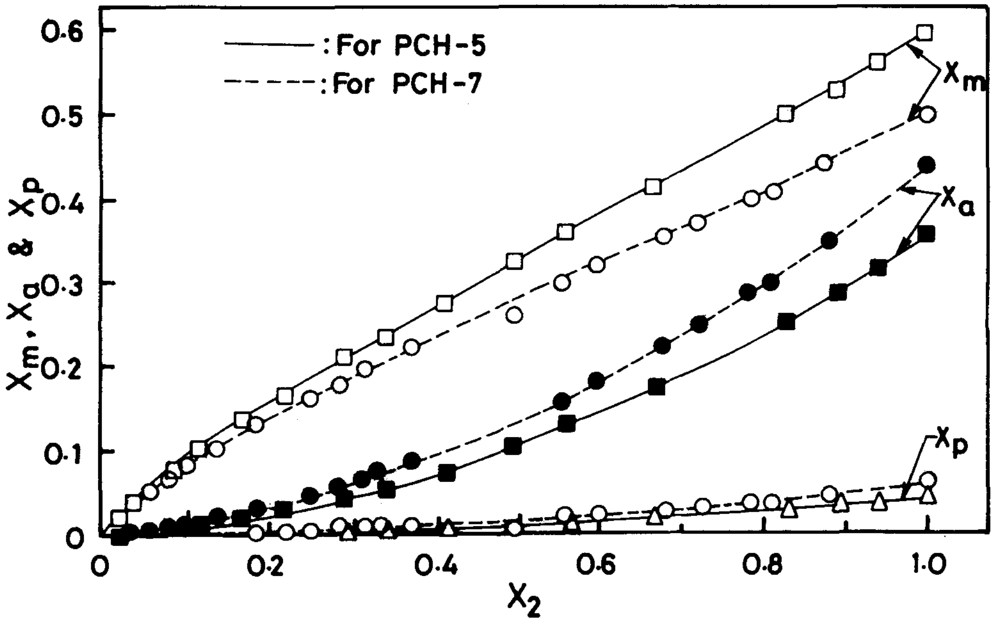

FIGURE 3 Monomer ($X_m$), Anti-parallel dimer ($X_a$) and Parallel dimer ($X_p$) mole fractions as a function of total solute mole fraction ($X_2$). Solid lines are results for PCH5 with $K_a$ = 0.96 and $K_p$ = 0.14; Broken lines are results for PCH7 with $K_a$ = 1.76 and $K_p$ = 0.22.

It should be noted here that the absolute values of the association constants ($K_a$,$K_p$) for PCH7 are almost double to those values obtained for PCH5. This is quite unexpected. Because the two molecules are very similar only differing by their chain lengths. This unexpected difference in the values of $K_a$ and $K_p$ of these two samples may be due to the limitations of the model used for the calculation of $K_a$,$K_p$; where dipole directions of the molecules in the dimers are taken as strictly parallel to each other. But in reality they may form dimers with the dipole moments making certain angle due to thermal fluctuations and packing constraints.

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