

Dielectric studies of molecular interactions in benzene solutions of 4-heptyl-4'-nitro-biphenyl

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Abstract

A study was made of the molecular association of 4-heptyl-4'-nitro-biphenyl (7NB4) in benzene, in the temperature range from 288 K to 323 K. With this aim both static linear and nonlinear dielectric properties were investigated. The experiments were carried out in the whole, solubility constrained, range of solubilities. The interpretation was only given for moderately diluted solutions, up to 0.3 molar fraction concentration. From the experimental values of both linear and nonlinear polarization the energy of intermolecular interactions was determined. In the adopted concentration range, a good agreement with the experiment was achieved when only binary interactions of 7NB4 molecules were assumed. Within experimental error, the obtained dipolar moment of the aggregates is zero meaning the antiparallel orientation of the molecules in the dimer. The most important and unexpected conclusions from these studies can be made when comparing the results with those of a similar study on the isomorphous compound 4-heptyl-4'-cyano-biphenyl (7CB4) which, in contrary to 7NB4, is mesogeneous. In pure 7CB4 one does not only have the nematic phase, but self-association in the dilute solution is much stronger, involving at least tetramers as well as the characteristic equilibrium constants between weakly and strongly polar multimers, which do not occur in 7NB4. Properties of the two compounds, and of the non-mesogeneous isomer 4-heptyl-3'-cyano-biphenyl (7CB3) are compared and discussed.

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1. Introduction

The structure of 4-heptyl-4'-nitro-biphenyl (7NB4) is very similar to the structure of 4-heptyl-4'-cyano-biphenyl (7CB4) which belongs to the known family of 4-*n*-alkyl-4'-cyano-biphenyls (*n*CB4), where mesophases are known to occur. However 7NB4 is not mesogenic and melts at 321.5 K to yield directly the isotropic liquid phase. The two molecules have large dipole moments of nearly the same magnitude. Although the dipolar interactions in the solid phase play a significant role, it remains to be explained what their importance is in the formation of mesophases.

The principal purpose of this study was to collect the information about molecular interactions and the structure of aggregates in benzene solutions 7NB4. This knowledge should contribute to an improved perception of the processes of molec-

ular association in liquids and the role of dipolar interactions in this process. We believe, that in the further perspective the studies of 7NB4 and the compounds studied earlier — including the non-mesogenic isomers 7CB3 [1] and 7CB4 [2,3] (Fig. 1) — will contribute to a better understanding of the processes responsible for the appearance of cooperative phenomena which effect, in the case of 7CB4, the nematic phase below 315.5 K. This subject will be discussed in a separate paper.

The main method used in the study of molecular interactions in these compounds was *Nonlinear Dielectric Effect* (NDE). This method is particularly useful in studying the weak inter- and intramolecular interactions. It uses the phenomena of molecular orientation in the electric field, therefore it can be applied in situations where molecular orientation of polar groups takes place, namely in gases, liquids and plastic crystals.

NDE describes the nonlinear dependence of electric polarization *P* on the electric field strength [4,5]. For practical purposes this nonlinearity is examined by monitoring the changes of electric permittivity $\Delta\epsilon$ — the quantity proportional to the

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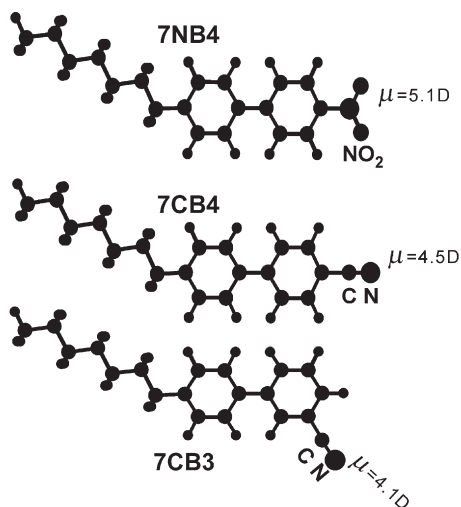


Fig. 1. Structure of biphenyls.

derivative of polarization P . Saturating the polarization in a strong electric field, described with the Langevin function, results in negative values of $\Delta\epsilon$. But, in the systems where the inter- or intramolecular equilibria exist, a positive effect, known as chemical effect, may dominate which is related to preferring objects with larger dipolar moment. Similar feature is observed in critical solutions, where the phase of larger polarizability is favoured [6,7].

Consequences of these processes are an increase of the total polarizability of the system. Describing the nonlinearity with the measurable quantity — the change of the electric permittivity $\Delta\epsilon = \epsilon_E - \epsilon$ effected by the electric field E — the nonlinearity of the medium can be expressed with the Piekara factor $\Delta\epsilon/E^2$. This quantity can be experimentally determined for numerous liquid systems if their electric conductivity is not too high. Then, using the general NDE theory [8], it is possible to determine the energy of the molecular interactions with reasonable accuracy.

The method of *Nonlinear Dielectric Effects* turned out to be a rich source of information on intermolecular interactions in the molecules with internal rotation [9–11], as well as on the proton transfer mechanism in the hydrogen bonded complexes [12–14]. The method was successfully applied in studies of the processes of molecular association in alcohol solutions [15,16] and lactams [17–19].

Similar properties were also observed for mesogenic compounds, in which both parallel or anti-parallel arrangement of molecules was found. These results were obtained with the dipole moment method, i.e. from linear polarization measurements [20–22]. However it ought to be emphasized that *Nonlinear Dielectric Method*, contrary to the linear measurements, is capable of unambiguous and precise distinction between the weak and strong polar complexes.

2. Experimental results

Measurements of the nonlinear properties of 4-heptyl-4'-nitro-biphenyl–benzene solutions were carried out with the pulse apparatus described earlier [5,12]. The electric field pulse length has been shortened down to less than 1 ms. It minimized the

amount of Joule heat to the extent making possible a correct measurement of the relative change of electric permittivity $\Delta\epsilon/\epsilon$ of the order of 10^{-7} – 10^{-6} for a liquid of electric resistivity $\sigma < 10^{-5}$ S/m with the accuracy around 3%. The frequency of the instrument was 5 MHz. For the correct interpretation of the results the frequency should be kept below the range of dipolar relaxation. Unfortunately, we do not have these data for 7NB4. We know however, that for similar but stronger interacting molecules 7CB4, the lowest relaxation frequency with rotations about the short axis is 50 MHz [23], hence we may safely assume that 7NB4 measurements have been performed sufficiently far away from the frequency of relaxation.

Measurement of electric permittivity (ϵ) of the sample (linear effect) were accomplished at 1 MHz with 0.05% accuracy with a Hewlett Packard 4192A LF impedance analyser. The density (d) of the solutions was measured with an ECOLAB densimeter, and refractive index (n) for the D sodium line with an Abbe refractometer. Both quantities were measured with an accuracy of 0.001.

The results of measurements of the electric permittivity (ϵ) and its changes ($\Delta\epsilon/E^2$) in a strong electric field E in the entire range of concentration available is shown in Fig. 2. The range of the higher concentrations ($f > 0.3$ molar fraction), where the results are obtainable only at the highest temperatures, was deliberately neglected in the analysis.

For the subsequent discussion it is convenient to express the experimental data (ϵ , d , n and $\Delta\epsilon/\epsilon$) as molar quantities: namely as the mean square of the dipolar moment ($\langle\mu^2\rangle$ — for linear polarizability) and the mean fourth power of the moment ($\langle\mu^4\rangle$ — for the nonlinear polarizability). These values are defined as follows:

$$\begin{aligned} \langle\mu^2\rangle &\equiv \frac{3kT}{r} \frac{\partial\langle\mu\rangle_E}{\partial F} \\ \langle\mu^4\rangle &\equiv -\frac{15k^3T^3}{r} \frac{\partial}{\partial(F^2)} \left(\frac{\partial\langle\mu\rangle_E}{\partial F} \right) = -5k^2T^2 \frac{\partial\langle\mu^2\rangle}{\partial(F^2)}, \end{aligned} \quad (1)$$

where k is a Boltzmann constant, T is absolute temperature, $\langle\mu\rangle_E$, usually expressed with Langevin function, is the mean value of the projection of dipole moment on the electric field E . F is the component of internal electric field along E direction, and $r = \mu/\mu_0$ is the ratio of the effective dipolar moment in the given medium to its magnitude in vacuum. The quantity r should not be confused with the Kirkwood correlation factor g . The two functions F and r depend on the applied internal field model. For the Onsager model [24] adopted in this work these functions become

$$F(\epsilon, n^2) = \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2} \quad \text{and} \quad r = \frac{(2\epsilon + 1)(n^2 + 2)}{3(2\epsilon + n^2)}. \quad (2)$$

The quantities $\langle\mu^2\rangle$ and $\langle\mu^4\rangle$ may also be expressed with the quantities measured in the experiment [16]. Adopting the Barriol and Wiesbecker [25] simplification they take the form

$$\begin{aligned} \langle\mu^2\rangle &= \frac{9\epsilon_0kT}{Nf} \frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2} V \\ \langle\mu^4\rangle &= -\frac{45\epsilon_0k^3T^3}{Nf} \frac{(2\epsilon^2 + n^4)(2\epsilon + n^2)^2}{\epsilon^4(n^2 + 2)^4} \frac{\Delta\epsilon}{E^2} V \end{aligned} \quad (3)$$

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