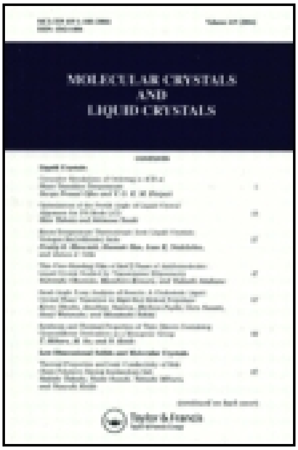

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DIMERIZATION OF POLAR MESOGENIC MOLECULES

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Abstract Dielectric polarization method has been used for studies of dipole-dipole self-association of n-pentylcyanobiphenyl (5-CB) and 4-(trans-4′-n-hexylcyclohexyl)isothiocyanatobenzene (6-CHBT) in non-polar solvents. A new approach to the dimer structure has been proposed.

INTRODUCTION

Based on the model by Kirkwood, the apparent dipole moment of polar molecules dissolved in non-polar solvents is given by

$$\mu_{app}^2 = g\,\mu_1^2 = \frac{9\,\varepsilon_0\,kT}{c\,N_A}\;\frac{(\varepsilon - \varepsilon_\infty)\,(2\varepsilon + \varepsilon_\infty)}{\varepsilon\,(\varepsilon_\infty + 2)^2} \qquad (1)$$

where μ_1 is the dipole moment of a free molecule, ε denotes the static electric permittivity, ε_∞ (often replaced by the square of the refractive index, n^2) is the permittivity measured at a frequency high enough to prevent orientational polarization, c is the nominal molar concentration of dipolar compound (in mole·dm^{-3}), N_A is the Avogadro constant and ε_0 = 8.85 pF/m. μ_{app} equals the dipole moment of a free molecule, μ_1, (i.e.)

Kirkwood correlation factor g = 1) and it does not depend on the concentration of dipolar substance only for non-interacting systems. In real molecular systems, the interactions lead to the formation of molecular aggregates which may orient as a whole in an electric field, and μ_{app} depends on concentration (and temperature). The shape of this dependence is related to the structure of the molecular aggregates formed.[1,2] Then μ_{app} can be expressed by the dipole moment of all chemical species i (μ_i) and their concentration (c_i):

$$c\ \mu^2_{app} = \sum c_i\ \mu^2_i \tag{2}$$

and the dipole moment value of a single molecules (monomer) can be obtained from the extrapolation of μ^2_{app} to the infinite dilution

$$(\mu^2_{app})_\infty = \mu^2_1\ . \tag{3}$$

RESULTS AND DISCUSSION

Experimental dependences of μ^2_{app} (c) obtained for solutions of 5-CB (in benzene) and 6-CHBT (in CCl_4) (points in Figure 1) indicate that the molecular aggregation processes lead here to intermolecular species with partially compensated dipole moment. The results have been interpreted with the assumption of monomer-dimer equilibrium in solutions under investigation:[3-7]

$$2\ A_1 \rightleftharpoons A_2\ ,\qquad K_2 = c_2/c_1^2\ , \tag{4}$$

where K_2 is the equilibrium constant, and c_1 and c_2 are the molar concentrations (in mole·dm^{-3}) of monomers and dimers, respectively. According to Eq. (4) the mass balance of investigated substance, $c = c_1 + 2\ c_2$, can be

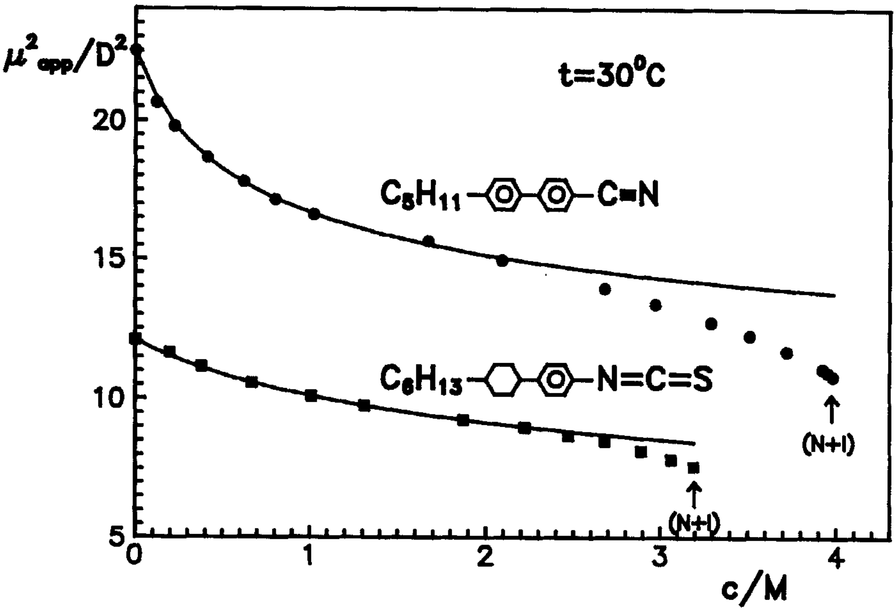

FIGURE 1 Experimental (points) and theoretical (solid lines) dependence of $\mu^2_{app}(c)$ for 5-CB and 6-CHBT dissolved in non-polar solvents. M denotes the concentration in mole·dm^{-3}.

expressed in the following form:

$$c_1 + 2 K_2 c_1^2 - c = 0 \tag{5}$$

In case of dimerization, Eq. (2) has the following form:

$$c \mu^2_{app} = c_1 \mu_1^2 + c_2 \mu_2^2 \quad . \tag{6}$$

The dipole moment values of a single molecule (μ_1) 5-CB and 6-CHBT, determined according to Eq. (3), are given in Table 1.

The values of dimerization constant K_2 and dipole moment of dimer μ_2 can be obtained from the best fitting of experimental data (points in Figure 1) and theoretical dependences $\mu^2_{app}(c)$ (Eqs.(5) and (6)).

Figure 1 shows that the monomer-dimer model (solid lines) works quite well only for concentrations up to about 2 M. The values of K_2 and μ_2 obtained from the fitting and the enthalpy of interactions are listed in Table I.

TABLE I Parameters of dimerization of 5-CB and 6-CHBT in non-polar solvents.

	5-CB + benzene (μ_1 = 4.77 D)		6-CHBT + CCl_4 (μ_1 = 3.48 D)	
t(^oC)	μ_2 (D)	$K_2(M^{-1})$	μ_2 (D)	$K_2(M^{-1})$
30^o	4.28	0.685	2.63	0.196
40^o	4.29	0.665	2.59	0.188
50^o	4.27	0.632	2.63	0.185
60^o	-	-	2.57	0.180
$\Delta H(kJ \cdot mole^{-1})$	-3.27 ± 0.54		-2.26 ± 0.29	

The most important conclusion resulting from these studies concerns dimers: lack of a full compensation of dipole moments means that the dimers have not strictly antiparallel structure. Interpretation of this fact presents some difficulties, since the values of μ_2 obtained from the best fitting of $\mu^2_{app}(c)$ refer to an "average" dimer. The non-zero dipole moments of dimers can be explained with several equivalent models, each of them agreeing with the experimental dependence of μ^2_{app} on concentration.

One of such models has been recently proposed by Toriyama and Dunmur.[7] In their approach the solution of polar nematic contains two kinds of dimers: parallel (μ_2 = 0) and antiparallel of the "head-tail" type

($\mu_2 = 2\mu_1$). The non-zero dipole moment obtained in experiment, according to this model, results from an equilibrium between these two rigid structures. The physical reality of this model seems to be doubtful. In a dynamic molecular system, like liquids (and nematics) the dipolar interactions, energy of which only slightly exceeds kT (Table I), lead to formation of the labile molecular aggregates, and the structure of such aggregates can be discussed in terms of average values.

Of course, for higher concentrations of mesogen the aggregates larger than dimers can be formed. However, our attempts to explain the observed considerable decrease of $\mu^2_{app}(c)$ above 2M by including higher aggregates with different polarity, did not provide any acceptable results.

In our approach, in a solution of polar substance, dimers of various structure are formed in such a way that the axis of dipoles form statistically different angles. In the dielectric experiment we observe an average dimer, polarity of which results from the fact that an average angle φ between axis of component dipoles is lower than 180^o (strictly antiparallel structure). For low and medium concentrations of dipoles, the value of this angle results from a competition between dipole-dipole interactions and thermal excitation. For higher concentration of dipoles the geometric packing of molecules seems to play a predominant role. It is obvious, that in case of elongated rod-like molecules of nematogen the packing should manifest itself in a distinct manner.

A considerable decrease in experimental value of μ^2_{app} in relation to theoretical expectations, observed for concentrations of mesogen higher than 2M (Figure 1),

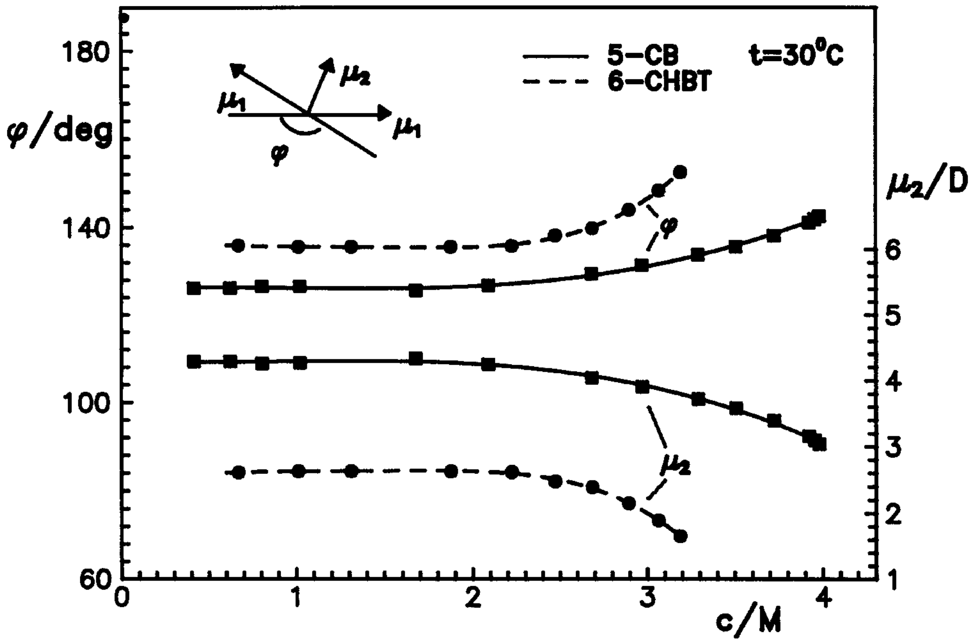

FIGURE 2 Dependence of φ and μ_2 values on concentration of 5-CB and 6-CHBT in non-polar solvents.

is in our opinion caused by a specific packing of molecules i.e. by increase of the angle φ between the component dipoles of dimer. Increasing value of the angle φ means a decrease of μ_2 (Figure 2). At constant value of K_2, the experimental dependence of $\mu^2_{app}(c)$ can be reproduced within the whole concentration range after adjusting the value of φ and thereby the dipole moment μ_2, for concentrations higher than 2M. The dimer becomes more and more antiparallel. The variations needed for explanation of this effect are relatively small (Figure 2). The value of φ angle amounting to about 130^0 for concentrations below 2M, increases up to about 150^0 just before the transition to the nematic phase.

Relative molar fractions of monomers and dimers as functions of concentrations of 5-CB and 6-CHBT in non-

-polar solvents are shown in Figure 3.

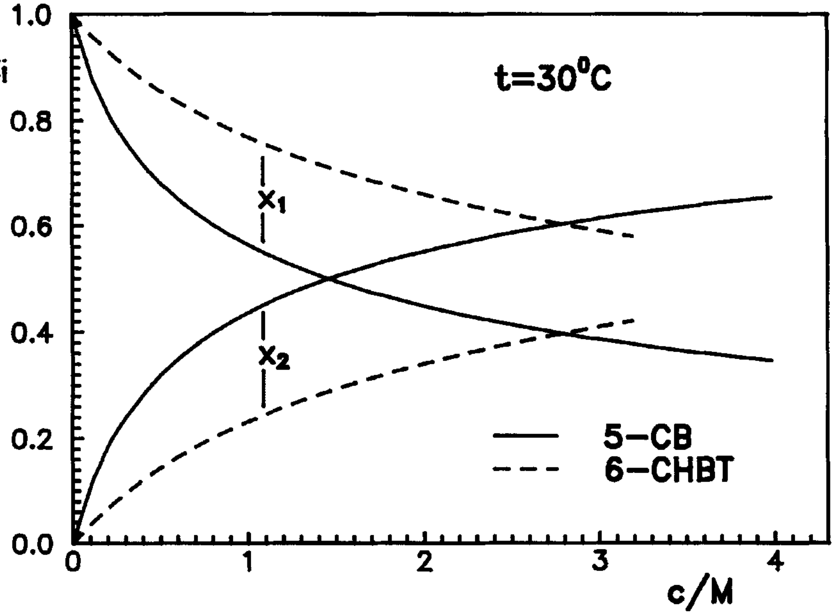

FIGURE 3 Relative molar fractions $x_i(=c_i/c)$ of monomers and dimers in 5-CB and 6-CHBT solutions.

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REFERENCES

1. J. Jadżyn, K. Prałat and P. Kędziora, J. Phys. Chem., 90, 2781 (1986).
2. J. Jadżyn and B. Żywucki, J. Mol. Structure, 145, 195 (1986).
3. M. J. Bradshaw and E. P. Raynes, Mol. Cryst. Liq. Cryst., 91, 145 (1983).
4. A. J. Leadbetter, J. C. Frost, J. P. Gaughan, G. W. Gray and A. Mosley, J. Phys.(Paris), 40, 375 (1979).
5. W. H. De Jeu, Physical Properties of Liquid Crystalline Materials (Gordon and Breach, 1980), p. 63.
6. J. O. Indekeu and A. N. Berker, Physica, 140 A, 368 (1986).
7. K. Toriyama and D. A. Dunmur, Mol. Phys., 56, 479 (1985); Mol. Cryst. Liq. Cryst., 139, 123 (1986).