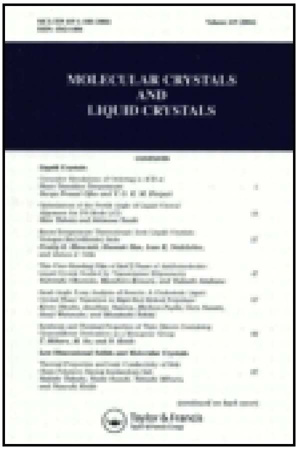

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Intermolecular Interaction in Binary Nematic Mixtures of 4-Methoxybenzylidene-4′-n-Butylaniline and n-Alkyl Alcohol

Shinichi Yano [a], Yasuomi Watanabe [a], Satoshi Taguchi [a] & Koichiro Aoki [a]

[a] Department of Synthetic Chemistry, Faculty of Engineering, Gifu University Yanagido 1-1, Gifu, 501-11, Japan

Version of record first published: 20 Apr 2011.

To cite this article: Shinichi Yano, Yasuomi Watanabe, Satoshi Taguchi & Koichiro Aoki (1982): Intermolecular Interaction in Binary Nematic Mixtures of 4-Methoxybenzylidene-4′-n-Butylaniline and n-Alkyl Alcohol, Molecular Crystals and Liquid Crystals, 90:1-2, 75-83

To link to this article: http://dx.doi.org/10.1080/00268948208076172

Mol. Cryst. Liq. Cryst., 1982, Vol. 90, pp. 75–83
0026-8941/82/9002-0075$06.50/0

Printed in the United States of America

Intermolecular Interaction in Binary Nematic Mixtures of 4-Methoxybenzylidene-4′-*n*-Butylaniline and *n*-Alkyl Alcohol

SHINICHI YANO, YASUOMI WATANABE, SATOSHI TAGUCHI
and KOICHIRO AOKI

*Department of Synthetic Chemistry, Faculty of Engineering, Gifu University
Yanagido 1-1, Gifu 501-11, Japan*

(*Received February 17, 1982; in final form June 30, 1982*)

The intermolecular interaction in nematic solvent was studied for binary nematic mixtures of MBBA with *n*-alkyl alcohol (carbon number of *n*-alkyl group, *n*, is between 4 and 14, and concentration of *n*-alcohol is 4 mol%) by dielectric relaxations. When *n* is between 5 and 9, a long range-intermolecular interaction decreased by adding *n*-alcohol, but underwent no change with *n*-alcohol, when *n* is larger than 10. From the above results, it was concluded that *n*-alkyl alcohols between $n = 5$ and 9 exist as rigid and non-linear shaped molecules in the nematic solvent, and that the higher alcohols above $n = 10$ are considerably flexible.

INTRODUCTION

Generally, binary nematic mixtures of nematic solvent with non-mesogenic solute have a transition temperature from nematic to nematic + isotropic phase, $T_{N \to N+I}$, and that from nematic + isotropic to isotropic phase, $T_{N+I \to I}$, with increasing temperature from the nematic phase. From the slope of $T_{N \to N+I}/T_{N+I \to I}$-solute concentration curve in the phase diagram, the past thermodynamical studies[1-3] make it possible to estimate an intermolecular interaction between nematic solvent and solute at an infinite dilute concentration of solute. The experimental results of many workers[1-4] indicated that the intermolecular interaction increased when the shape of solute is rigid and linear, and decreased when non-linear.

Recently[5-7] we indicated that the dielectric relaxation method can evaluate the intermolecular interaction in binary nematic mixtures by using the equation,

$$Q = \Delta H_L - \Delta H_H(\Delta H_\eta), \tag{1}$$

derived from the Meier-Saupe theory.[8] Q, ΔH_L, ΔH_H and ΔH_η are nematic potential, activation enthalpy of lower frequency relaxation (L relaxation), activation enthalpy of higher frequency relaxation (H relaxation) and activation enthalpy of viscosity at the isotropic phase, η, respectively, provided that the L relaxation means the relaxation appearing in the lower frequency range between the two anisotropic dielectric relaxations which have the oriented nematic liquid crystals, and that the H relaxation represents that in the higher frequency range. By the dielectric method, therefore, we can evaluate the intermolecular interaction for nematic ordering in nematic solvent, itself (a long range-intermolecular interaction by Q and a short range-intermolecular interaction by ΔH_H or ΔH_η) and the interaction at arbitrary solute concentrations. In other words, the dielectric method serves to elucidate how the solute changes the intermolecular interaction for nematic ordering. The above characteristic points distinguish the dielectric method from the thermodynamical method in evaluating the interaction.

In this paper, we report studies of the intermolecular interaction in binary nematic mixtures of 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) and *n*-alkyl alcohol by the dielectric relaxations. It is known that *n*-alkyl alcohol has a rigid and elongated conformation (a planar zig-zag conformation) in a crystalline state but not always in a solution. Since the intermolecular interaction in nematic solvent is sensitively affected by the shape of solute molecule, the study of intermolecular interaction by dielectric relaxation method must clarify the shape of *n*-alkyl alcohol in nematic solvent. It is of interest to examine the shape of *n*-alkyl alcohol in nematic solvent as a function of number of carbon atom in *n*-alkyl group, *n*, because the molecular ordering in nematic solvent, of course, lies between that of a crystalline solid and that of an isotropic liquid.

EXPERIMENTAL

MBBA was synthesized and purified by the same procedure as described previously.[5] A homologous series of *n*-alkyl alcohol were purified

TABLE I

List of samples.

Sample	Solute[a]	Conductivity at 25°C (10^{-10}) $\Omega^{-1}\cdot cm^{-1}$	Density at 63°C g/ml
MBBA		9.5	1.012
B-4	*n*-butyl alcohol	1.4	1.010
P-4	*n*-pentyl alcohol	3.7	1.010
H-4	*n*-hexyl alcohol	4.8	1.009
HP-4	*n*-heptyl alcohol	5.0	1.010
O-4	*n*-octyl alcohol	4.7	1.007
N-4	*n*-nonyl alcohol	2.1	1.008
D-4	*n*-decyl alcohol	1.8	1.005
U-4	*n*-undecyl alcohol	3.3	1.006
DO-4	*n*-dodecyl alcohol	2.3	1.007
TD-4	*n*-tetradecyl alcohol	1.1	1.005

[a] Concentrations of solute are 4 mol% in all samples.

by distilling just before use. The binary mixtures were carefully prepared by mixing each component under a dry nitrogen atmosphere at a temperature just above the clearing temperature. The samples used are listed in Table I.

Dielectric and viscosity measurements were carried out in the way described previously.[5,6] Dielectric constant, $\epsilon'_{\parallel}$, and the loss, $\epsilon''_{\parallel}$, in the parallel direction to the applied magnetic field of 4 kOe were measured at frequencies between 300 Hz and 5 MHz. Densities were measured by a Lipkin–Davidson pychnometer.

RESULTS AND DISCUSSION

Figure 1 shows dependence on frequency of $\epsilon''_{\parallel}$ for U-4 at several temperatures. The L relaxation is observed near 1 MHz. The L relaxations were observed in all the samples used. The Arrhenius plots for the L relaxation in various samples are shown in Figures 2 and 3. The L relaxation shifts to lower temperatures with adding *n*-alkyl alcohol in MBBA solvent. The activation enthalpies, ΔH_L, and the relaxation times, τ_L, for the L relaxation in various samples are listed in Table II. The Arrhenius plots for viscosity at the isotropic phase, η, in several samples are shown in Figures 4 and 5. The values of η show little dependence on *n* of *n*-alcohol. The activation enthalpies for η, ΔH_η, and the values of Q obtained by the Eq. (1) are also listed in Table II. Plots

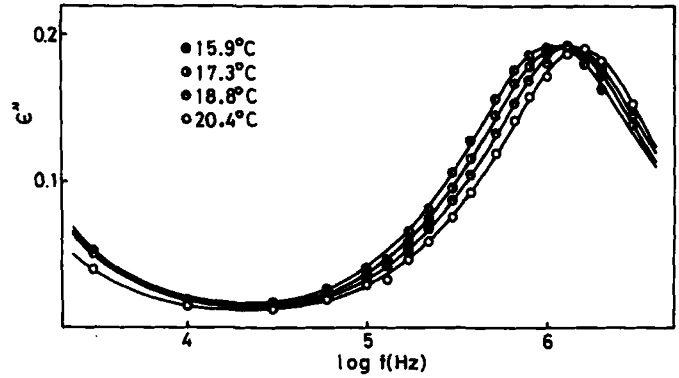

FIGURE 1 Frequency dependences of dielectric loss, $\epsilon''_\parallel$, for U-4 at several temperatures.

of ΔH_L, $\Delta H_\parallel$ and Q versus *n* are shown in Figure 6. The values of Q decrease with increasing *n* from *n* = 5, and exhibit a minimum near *n* = 8. In the values of *n* above 10, the value of Q is approximately equal to that for MBBA. These results mean that a long range-intermolecular interaction in nematic solvent decreases in *n*-alkyl alcohols between *n* = 5 and 9, but undergo no change with the higher alcohols above *n* = 10, namely the molecular ordering in nematic solvent is disturbed by *n*-alcohol between *n* = 5 and 9, but not by the higher alcohol

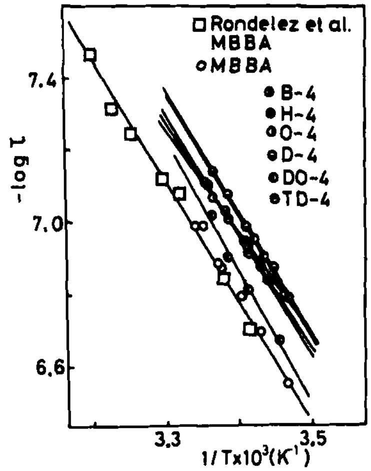

FIGURE 2 The Arrhenius plots of L relaxations in various samples.

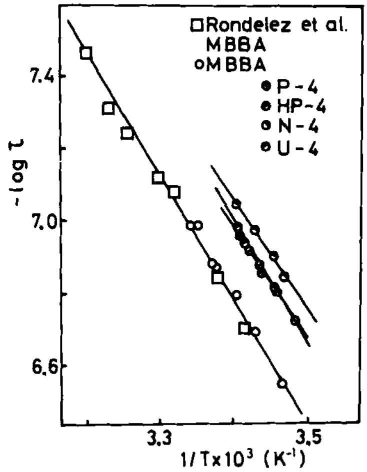

FIGURE 3 The Arrhenius plots of L relaxations in various samples.

from $n = 10$. Ultra-violet spectra of dilute MBBA in the homologous series of n-alkyl alcohol were measured with a UV spectrometer (Japan Optics Co. Type UVDEC-1). The absorptions at about 284 and 323 nm were observed to which a local excited configuration and a charge transfer configuration mainly contribute, respectively.[9] The ratio of the intensities of the two absorptions is known to be related to an angle between the two coplanar planes governed by the two benzene rings, respectively.[9] The intensities and the frequencies of the two absorptions were almost same in all n-alcohol solvents. Therefore, even if a chemi-

TABLE II

Values of τ_L, ΔH_L, ΔH_η and Q in various samples.

Sample	τ_L at 26.2°C (10^{-18})	ΔH_L kJ/mol	ΔH_η kJ/mol	Q kJ/mol
MBBA	10.3	63.2	33.5	29.7
B-4	8.26	67.3	32.9	34.4
P-4	6.98	56.1	32.9	23.2
H-4	7.05	55.2	33.2	22.0
HP-4	6.98	54.4	32.9	21.5
O-4	7.28	51.9	33.2	18.7
N-4	5.86	55.9	32.9	23.0
D-4	5.97	62.3	33.2	29.1
U-4	6.25	62.7	32.9	29.8
DO-4	6.03	62.5	32.9	29.6
TD-4	6.91	61.9	32.9	29.0

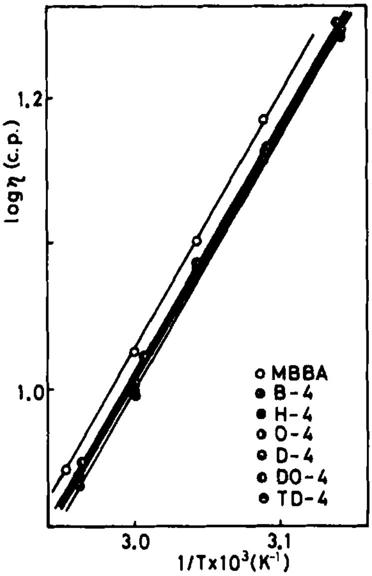

FIGURE 4 The Arrhenius plots of viscosities at the isotropic state, η, in various samples.

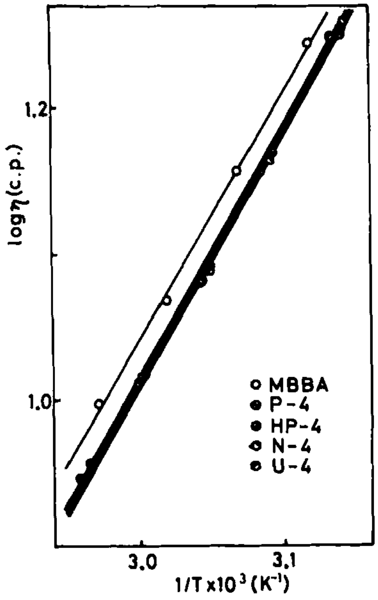

FIGURE 5 The Arrhenius plots of viscosities at the isotropic state, η, in various samples.

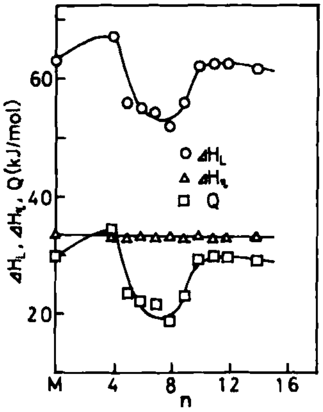

FIGURE 6 Plots of ΔH_L, ΔH_η and Q vs. number of carbon atom in *n*-alkyl alcohol, *n*, for MBBA-*n*-alkyl alcohol system. M: MBBA.

cal bond between MBBA and *n*-alcohol, for example as a hydrogen bond, yields in this system, it seems to undergo no change with *n*. Consequently, the dielectric results suggest that *n*-alcohol exists as rigid and non-linear shaped molecules in the nematic solvent, when *n* is between 5 and 9. Furthermore, above $n = 10$, *n*-alcohol may become flexible and may begin to have a nature of polymeric chain. The effect of polymeric solute on the intermolecular interaction between nematic solvent and solute has been studied in several binary systems of nematic liquid crystals with flexible polymer from the phase diagram by several workers.[10,11] Kronberg, Bassingnana and Patterson[10] indicated that the polymeric solute (polyethylene oxide and polystyrene) trends to destroy the intermolecular interaction but the contribution per unit segment of polymeric solute to the intermolecular interaction decreases with increasing molecular weight of polymer. Very recently, Debault, Casagrande and Veyssie[11] pointed out that the polymeric solute disturbs the nematic ordering intensely, when the polymeric solute has a coil conformation. The present results suggest that the flexible alcohols ($n = 10$–14), the molecular length of which are comparable to that of MBBA solvent, pack in the nematic solvent not to disturb the nematic ordering.

The change of nematic–isotropic temperature, T_{N-I}, with concentration of *n*-alcohol in MBBA-*n*-alkyl alcohol system was reported in 1970 by Cladis, Rault and Burger.[12] The depression of T_{N-I} per CH_2 group in *n*-alcohol, $\Delta T_{N-I}/CH_2$, decreases with increasing *n* (proportional to *n* up to $n = 5$ and gradually above $n = 5$) but increases

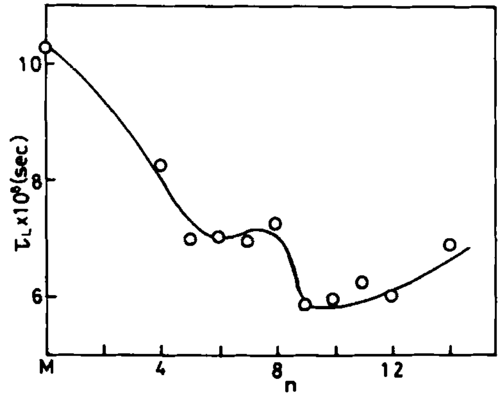

FIGURE 7 Plots of relaxation time for L relaxation at 26.2°C, τ_L, vs. number of carbon atom in *n*-alkyl alcohol, *n*. M: MBBA.

slightly above $n = 14$, the length of which is nearly equal to that of MBBA molecule. They proposed that the increase above $n = 14$ is due to the flexibility of *n*-alkyl chains. Referring their results qualitatively to the HJL theory *et al.*,[1-3] the shape of *n*-alcohol molecule in nematic solvent may become more linear with increasing *n* when *n* is between 1 and 4, and may be rather non-linear shaped when *n* is between 5 and 14. Their results are somewhat different in part from our dielectric results, and the reason may be explained by the fact that the dielectric method detects the intermolecular interaction between nematic molecules in nematic solvent, while the thermodynamical method evaluates that between nematic solvent and solute.

Plots of the relaxation time for the L relaxation at 26.2°C, τ_L, versus *n* are shown in Figure 7 (also see Table II). The values of τ_L decrease with increasing *n* and exhibit a bumpy peak between $n = 5$ and 9. The latter peak may be connected with the abnormal decrease of Q.

In this paper, it was concluded that *n*-alkyl alcohol exists as rigid and non-linear shaped molecules in nematic solvent when *n* is between 5 and 9, and is considerably flexible when *n* is larger than 10.

References

1. R. L. Humphries, P. G. James and G. R. Luckhurst, *Symp. Faraday Soc.*, **5**, 107 (1971).
2. G. I. Agren and D. E. Martrie, *J de Phys.* (*Paris*), **36**, C1-141 (1975).
3. G. I. Agren, *Phys. Rev.*, **A11**, 1040 (1975).

4. K. Fujimura, S. Mita, S. Kondo and M. Takeda, *Mol. Cryst. Liq. Cryst.*, **54,** 191 (1979).
5. S. Yano, Y. Hayashi and K. Aoki, *J. Chem. Phys.*, **68,** 5214 (1978).
6. S. Yano, K. Terashima, Y. Watanabe and K. Aoki, *J. de Phys.* (*Paris*), **C3,** 322 (1979).
7. S. Yano, Y. Watanabe, K. Terashima and K. Aoki, *Mol. Cryst. Liq. Cryst.*, **66,** 75 (1981).
8. G. Meier and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **1,** 515 (1966). A. Martin, G. Meier and A. Saupe, *Symp. Faraday Soc.*, **5,** 119 (1971).
9. for example, see R. Akaba, K. Tokumura and T. Kobayashi, *Bull. Chem. Soc. Japan*, **53,** 1993 (1980).
10. B. Kronberg, I. Bassignana and D. Patterson, *J. Phys. Chem.*, **82,** 1714 (1978).
11. A. Debault, C. Casagrande and M. Veyssie, *Mol. Cryst. Liq. Cryst.*, **72,** 189 (1982).
12. P. E. Cladis, J. Rault and J. P. Burger, *Liquid Crystals, 3 Part II*, ed. G. H. Brown and M. M. Labes, Gordon and Breach, London (1972) p. 701.