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Abstract

Positron lifetimes in the isotropic phases of chiral nematic liquid crystal formulations and their mixtures up to the racemic level have been measured. The lifetime spectra for all liquid crystal systems were analyzed into three components. Although the individual spectra in the left- and right-handed components are identical, their racemic mixtures exhibit much larger orthopositronium lifetimes, which indicates the presence of larger microvoids. This result is consistent with the reportedly higher thermodynamic stability and color play range in the racemic mixtures of chiral nematic liquid crystals.

Introduction

Liquid crystals are an interesting phase of matter. They retain some of the features of the solid state well beyond their melting points. They are used extensively in display devices, image converters, optical switching elements, and thermal indicators. They have also been used in aerodynamic studies as indicators of flow transition and flow separation on test model surfaces. Unfortunately, most of the unencapsulated chiral nematic liquid crystals applied on test surfaces erode away under the influence of the applied shear stress. Encapsulation of liquid crystals in appropriate matrices, on the other hand, reduces their sensitivity to the external influences. As a result, there is a strong need for the development of liquid crystal systems that will have strong steric interactions with the model surface and will not be washed away under the impact of tangential forces on the model surfaces. In an effort to address this problem, the microstructural characteristics of several monomer liquid crystal systems were evaluated. Positrons were used as probes for measuring microcavity dimensions in TM74A and TM74A* mixtures supplied by BDH,[1] and chiral nematic (right-handed) and cholesteryl ester (left-handed) liquid crystals supplied by Hallcrest.[2] The results of this study are described in the following sections.

Experimental Procedure

Preparation of Liquid Crystal Systems

Two types of liquid crystal systems were investigated: (1) TM74A, a low-temperature color play formulation, and its racemized analogue, TM74B; (2) BN/R20CIW (right-handed chiral nematic) and CN/R20CIW (left-handed cholesteryl ester) liquid crystals. The phase transition temperatures of these systems are summarized in tables I and II. Figures 1 and 2 are typical phase diagrams for mixtures of pure chiral nematic systems.

Different mixtures of left- and right-handed systems were prepared by mixing them at room temperature. Each mixture was then heated to about 80°C (in the isotropic liquid phase), held there for 15 min, and kept well stirred. The mixture was then allowed to cool down slowly to room temperature and was kept overnight before making the positron lifetime measurements. Positron lifetime measurements were made in TM74A samples before and after heating them to 80°C. All lifetime components were equal within experimental errors. Thus, heating the constituent formulations to 80°C for producing stable mixtures of liquid crystalline systems does not affect their intrinsic structures.

Positron Lifetime Measurements

Figure 3 shows the target chamber for holding the β^+ source and the liquid crystal sample. A 50-μC Na^{22} source was sealed between two 2.54-μm-thick Kapton[3] films. The source bag was then sandwiched between two 2.24-cm × 2.00-cm × 0.025-cm aluminum wafers. The wafers have 0.45-cm-diameter holes to permit positrons to escape into the liquid crystal mixture that surrounds the source assembly. Positron lifetime measurements were made at room temperature by using a fast-fast coincidence measurement system. (See ref. 1.) The coincidence system time resolution is ≈225 psec. Figure 4 shows a typical lifetime spectrum in TM74A liquid crystal formulations. Lifetime spectra were analyzed by using PAPLS (ref. 2) and POSFIT-EXTENDED (ref. 3) computer programs. In all cases, 3-component analyses gave the best fits to the experimental spectra.

Results

Positron lifetime measurements were made in mixtures of TM74A and TM74B liquid crystals at room temperature (23°C). As can be seen from the phase transition temperatures summarized in table I, the test mixtures were in the isotropic liquid phase. The composition of the mixtures ranged from 100-percent (pure) TM74A to 100-percent (pure) TM74B. The results of the 3-component lifetime spectral analysis are summarized in table III and illustrated in figures 5 to 10. It is evident that the first-component lifetime τ_1 and its intensity I_1 are independent of the ratio of TM74A to TM74A* in the

[1] BDH Ltd., Poole, BH12 4NN, England.

[2] Hallcrest, Glenview, IL.

[3] Kapton polyimide resin, manufactured by E. I. du Pont de Nemours & Co., Inc.

mixture. The second-component lifetime τ_2, however, increases as we go from pure TM74A to the racemic mixture, TM74B, though its intensity I_2 remains essentially constant. The second-component lifetime is related to the depth of the defect where the positron was trapped before its annihilation with a free electron. Deeper defects lead to larger values of τ_2. Just as with τ_2 and I_2, the third-component lifetime τ_3 increases as we go from pure TM74A to the racemic mixture, TM74B, but its intensity I_3 remains essentially constant.

The third-component lifetime τ_3 is related to the size of the microvoid, where orthopositronium atoms are trapped, by the following equation (ref. 4):

$$\frac{1}{2\tau_3} = 1 - \frac{R}{R_0} + \frac{1}{2\pi}\left(\sin 2\pi\frac{R}{R_0}\right) \qquad (1)$$

where

τ_3	third-component lifetime, nsec
R	microvoid radius, nm
R_0	$(R + 0.1656)$, nm

The microvoid volume V_f is given by $\frac{4}{3}\pi R^3$.

The values of V_f for different concentrations of TM74A in the TM74A + TM74B mixture have been calculated using equation (1). The results are summarized in table III and are illustrated in figure 11. It is evident that the racemic mixture (TM74B) has much larger microvoids than the pure TM74A formulation. This result indicates that the racemic mixtures have larger microvoids than their constituent formulations. This fact was further verified by making positron lifetime measurements in BN/R20CIW (right-handed liquid crystal), CN/R20CIW (left-handed liquid crystal), and their racemized mixture. As indicated in table II, all these systems are in cholesteric liquid crystalline phase at the room temperature where positron lifetime measurements were made. The positron lifetime results are summarized in table IV. It is evident that while the left- and right-handed formulations have similar spectra, their racemic mixture has longer lifetimes for the third (τ_3) and second (τ_2) components.

Discussion

The positron lifetime measurements in mixtures of variable relative concentrations of TM74A and TM74B chiral nematic liquid crystals indicate that the second-component lifetime τ_2 increases from 438 ± 11 psec to 592 ± 22 psec, whereas the third-component lifetime τ_3 increases from 2732 ± 18 psec to 3121 ± 41 psec, as one goes from a pure formulation to its racemized analogue. The increase in τ_2 implies deeper positron defects in racemized mixtures. The increase in τ_3, on the other hand, indicates that microvoids are larger in the racemized mixture. These results are quite consistent with the reportedly higher thermodynamic stability and color play ranges in racemized mixtures of such formulations (ref. 5). Because of the asymmetry of the chiral molecules, the steric interactions in racemized states are stronger than in the nonracemized states. These stronger steric interactions among the component molecular systems lead to a higher degree of entanglements which result in larger microvoids in the racemized mixtures. The entangled systems also require more thermal energy to unwind the helix; this increases their color play ranges and the transition temperatures.

Conclusions

From the positron lifetime results discussed in this report, the following general conclusions can be drawn:

1. The racemic liquid crystal formulations have deeper defects than their constituent systems.
2. The racemic formulations have almost 25-percent larger microvoids than the nonracemized liquid crystal components.

These results are consistent with the higher thermodynamic stability and color play ranges observed in the racemized mixtures of cholesteric liquid crystal formulations.

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Table I. Summary of Phase Transition Temperatures of TM74A and TM74B[1] Systems

[S_A = Smectic A
Ch = Cholesteric
I = Isotropic liquid]

Liquid crystal system	Transition temperature, °C	
	S_A-Ch	Ch-I
TM74A	–32.6	15.9
TM74B	–32.3	16.2

[1]50-50 mixture of TM74A and its complex conjugate TM74A*.

Table II. Summary of Phase Transition Temperatures of BN/R20CIW (Right-Handed) and CN/R20CIW (Left-Handed) Liquid Crystals

[S_A = Smectic A
Ch = Cholesteric
I = Isotropic liquid]

Liquid crystal system	Transition temperature, °C	
	S_A-Ch	Ch-I
BN/R20CIW	18.5	41.5
CN/R20CIW	16.0	43.0

Table III. Positron Lifetime Parameters in Mixtures of TM74A and TM74B

$$\begin{bmatrix} \tau_i = \text{Lifetime of } i\text{th component} \\ I_i = \text{Intensity of } i\text{th component} \\ V_f = \text{Microvoid volume} \end{bmatrix}$$

Percent TM74A	τ_1, psec	I_1, percent	τ_2, psec	I_2, percent	τ_3, psec	I_3, percent	V_f, A^{3*}
50.00	242 ± 13	44.3 ± 5.0	592 ± 22	39.5 ± 5.0	3121 ± 41	16.3 ± 1.0	213.2
58.19	250 ± 5	45.2 ± 5.0	568 ± 9	38.3 ± 9.0	3097 ± 15	16.5 ± 1.0	209.1
62.72	268 ± 2	51.5 ± 5.0	568 ± 30	32.5 ± 5.0	3072 ± 44	16.1 ± 1.0	207.7
71.2	264 ± 5	59.8 ± 2.0	512 ± 12	33.7 ± 2.0	2994 ± 18	16.5 ± 1.0	198.3
74.36	266 ± 10	52.4 ± 4.0	528 ± 27	31.7 ± 4.0	2953 ± 41	15.9 ± 1.0	193.2
77.40	277 ± 11	54.7 ± 5.0	509 ± 34	29.2 ± 5.0	2906 ± 41	16.1 ± 1.0	188.1
80.16	271 ± 5	51.7 ± 2.0	482 ± 14	31.9 ± 2.0	2912 ± 19	16.4 ± 1.0	189.3
83.85	273 ± 10	55.4 ± 4.0	454 ± 33	28.4 ± 4.0	2905 ± 47	16.1 ± 1.0	188.0
87.38	282 ± 12	57.5 ± 6.0	445 ± 42	26.9 ± 5.0	2818 ± 52	15.6 ± 1.0	178.1
90.50	247 ± 14	44.1 ± 5.0	455 ± 23	39.7 ± 5.0	2861 ± 41	16.2 ± 1.0	184.2
93.18	260 ± 15	49.7 ± 2.0	442 ± 10	34.5 ± 2.0	2708 ± 17	15.8 ± 1.0	167.3
95.15	233 ± 17	36.7 ± 6.0	457 ± 19	46.5 ± 5.0	2649 ± 38	16.8 ± 1.0	160.3
100.0	259 ± 5	47.0 ± 2.0	438 ± 11	36.9 ± 2.0	2732 ± 18	16.1 ± 1.0	169.6

*V_f has been calculated from the microvoid radius R in equation (1).

Table IV. Positron Lifetime Parameters in BN/R20CIW and CN/R20CIW Liquid Crystals

$$\begin{bmatrix} \tau_i = \text{Lifetime of } i\text{th component} \\ I_i = \text{Intensity of } i\text{th component} \end{bmatrix}$$

	τ_1, psec	I_1, percent	τ_2, psec	I_2, percent	τ_3, psec	I_3, percent
100 percent BN/R20CIW	264 ± 4	48.4 ± 2.0	512 ± 8	34.5 ± 2.0	3189 ± 13	17.1 ± 1.0
100 percent CN/R20CIW	272 ± 6	49.0 ± 3.0	512 ± 12	33.4 ± 3.0	3223 ± 15	17.6 ± 1.0
Nematic (60 percent BN + 40 percent CN)	269 ± 9	53.8 ± 4.0	559 ± 30	28.3 ± 4.0	3265 ± 42	17.9 ± 1.0

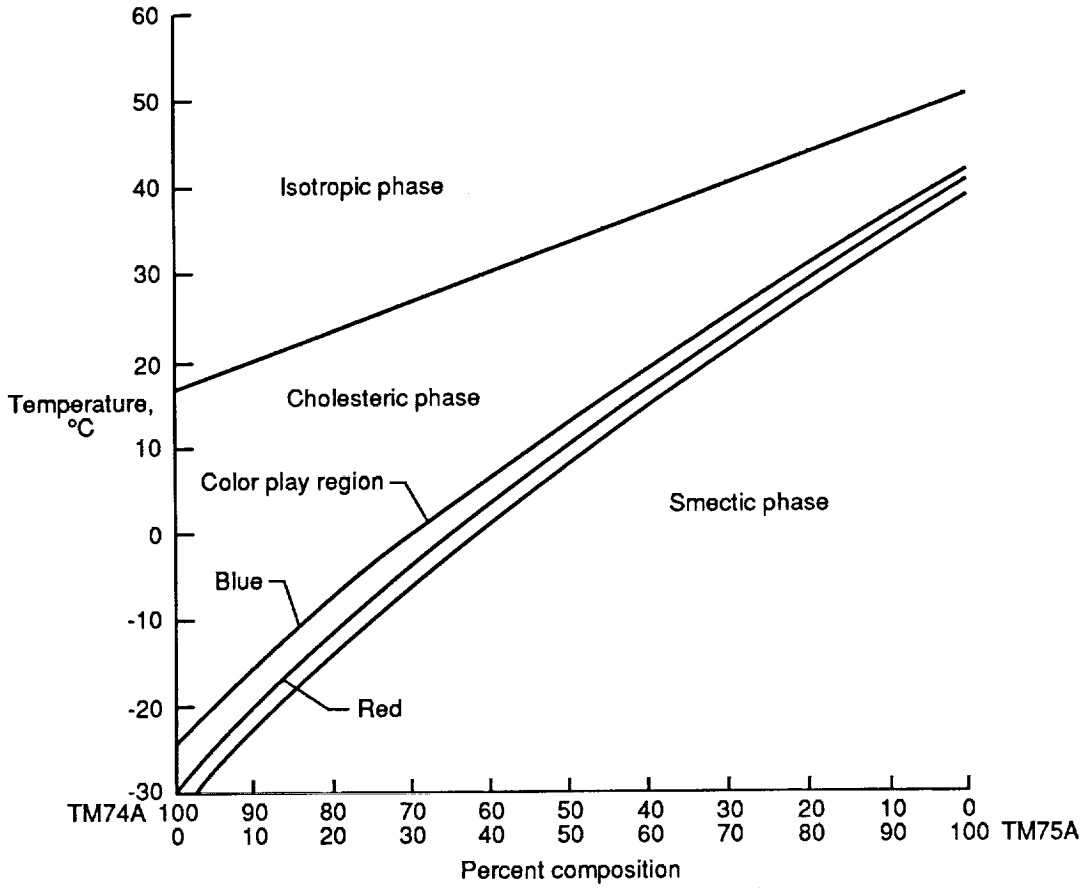

Figure 1. Phase diagram for mixtures of TM74A and TM75A. (TM74A and TM75A are low- and high-temperature color play formulations, respectively. Their chemical compositions are identical.)

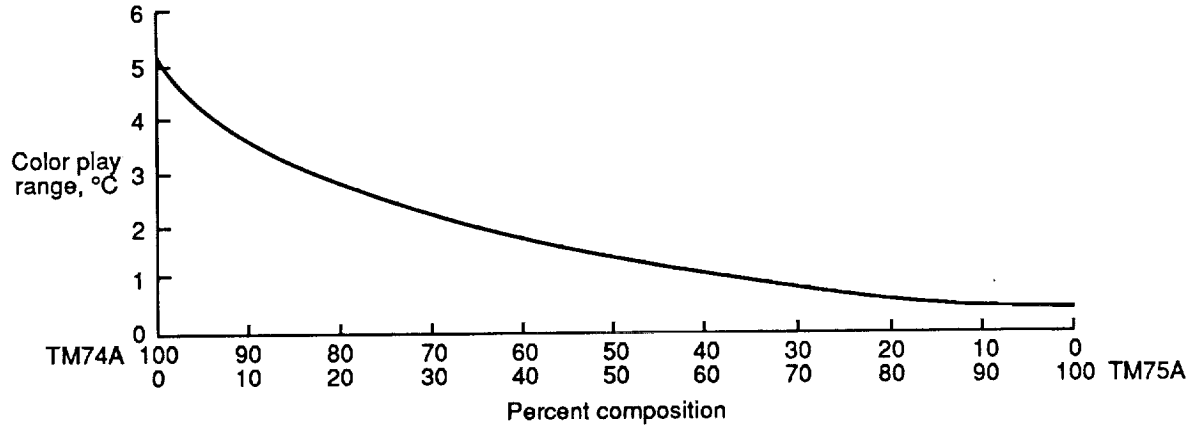

Figure 2. Color play range for mixtures of TM74A and TM75A. (TM74A and TM75A are low- and high-temperature color play formulations, respectively. Their chemical compositions are identical.)

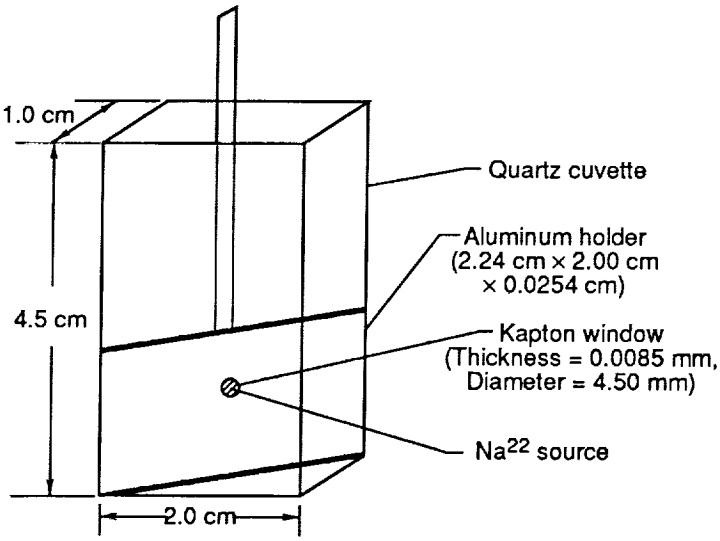

Figure 3. Schematic of liquid crystal target and source assembly.

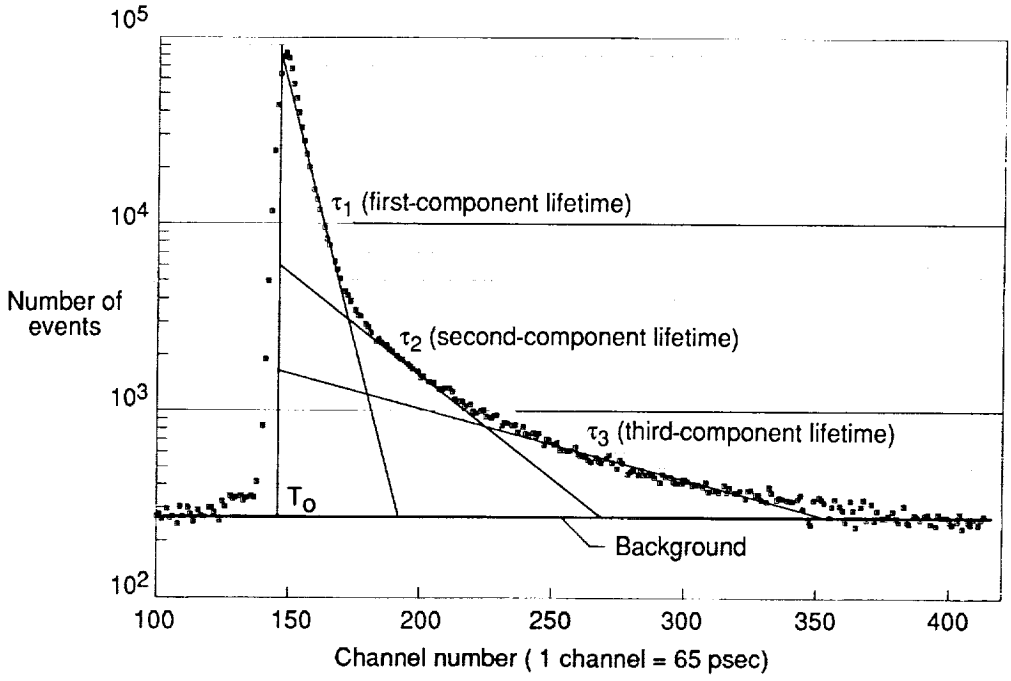

Figure 4. Typical positron lifetime spectrum in TM74A liquid crystal.

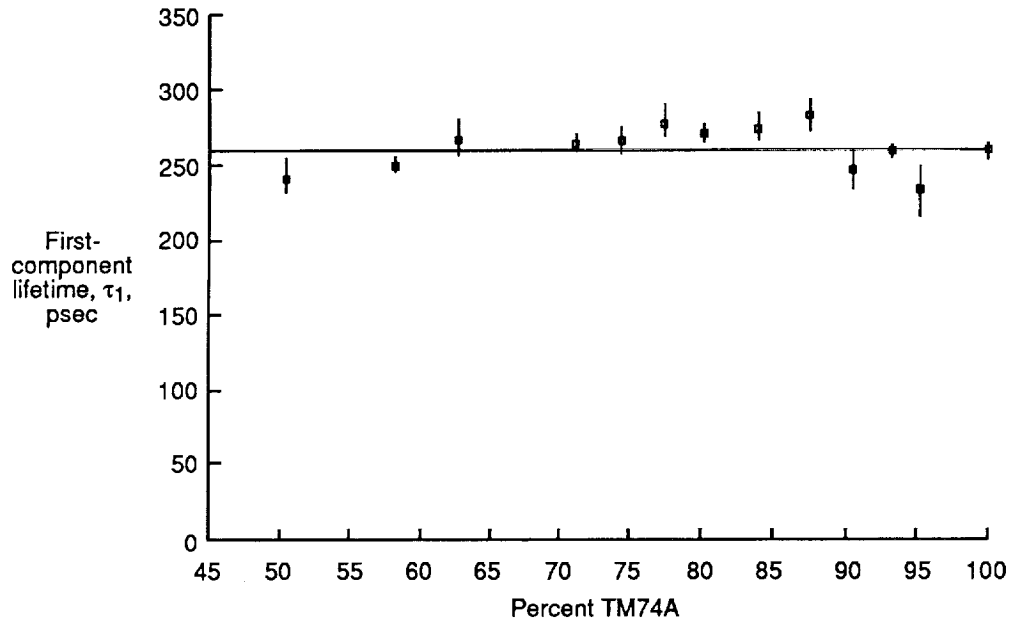

Figure 5. First-component lifetime versus percent of TM74A in mixture of TM74A and TM74A*.

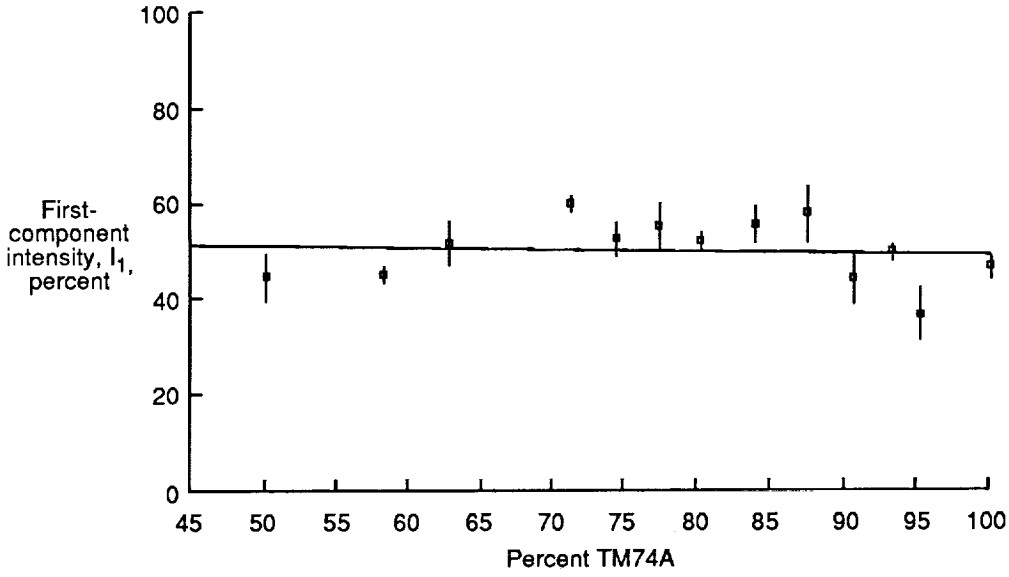

Figure 6. First-component intensity versus percent of TM74A in mixture of TM74A and TM74A*.

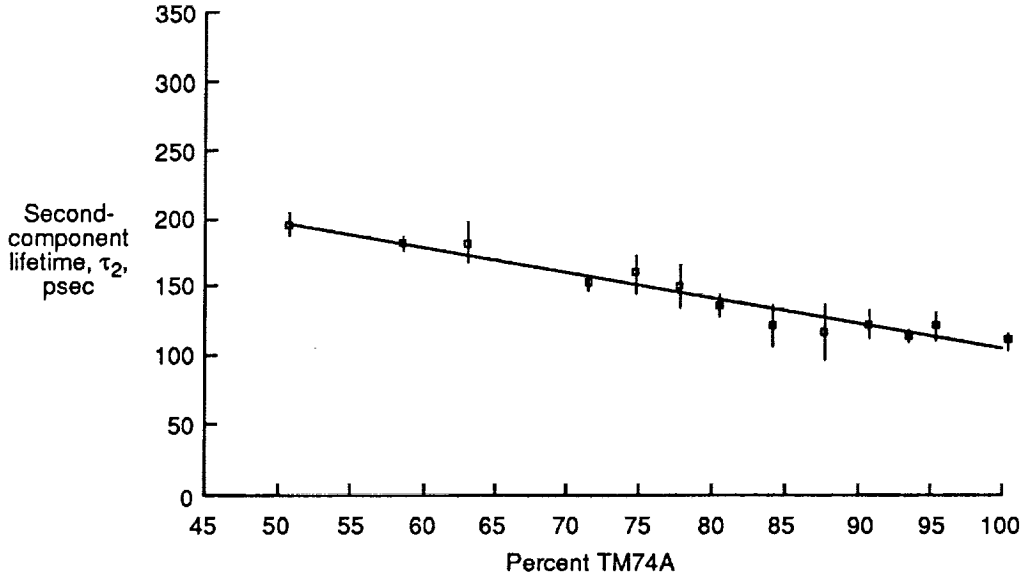

Figure 7. Second-component lifetime versus percent of TM74A in mixture of TM74A and TM74A*.

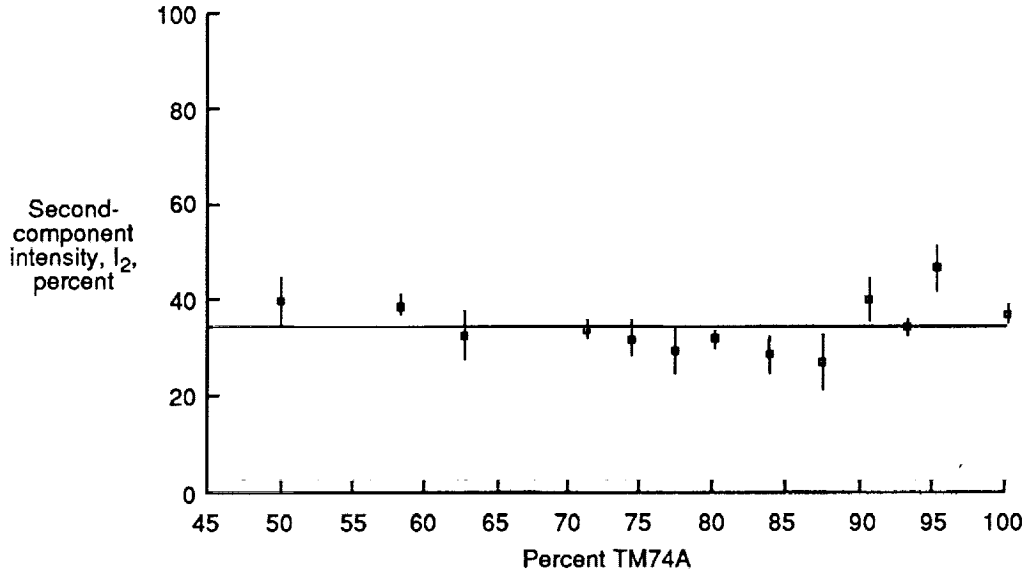

Figure 8. Second-component intensity versus percent of TM74A in mixture of TM74A and TM74A*.

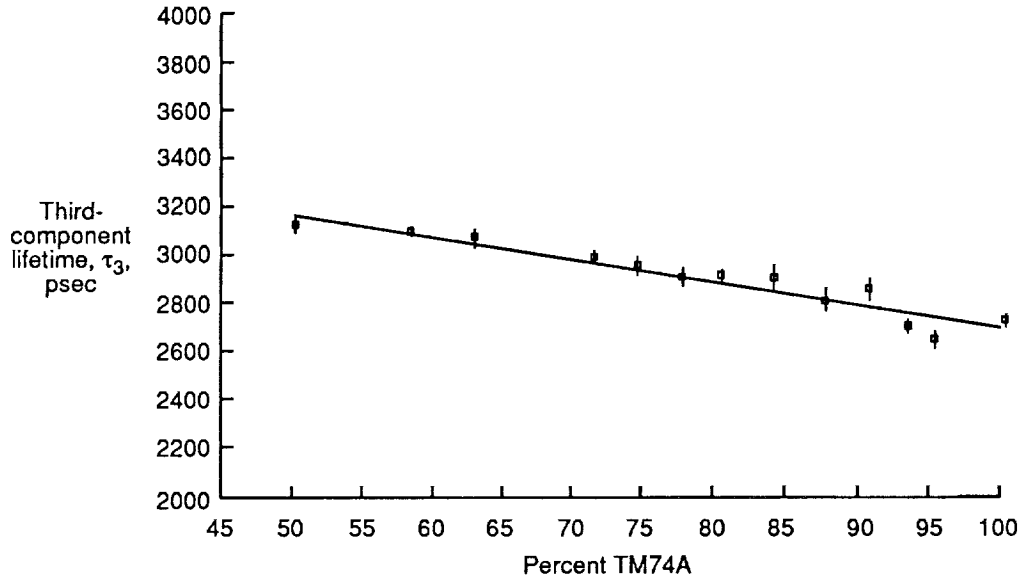

Figure 9. Third-component lifetime versus percent of TM74A in mixture of TM74A and TM74A*.

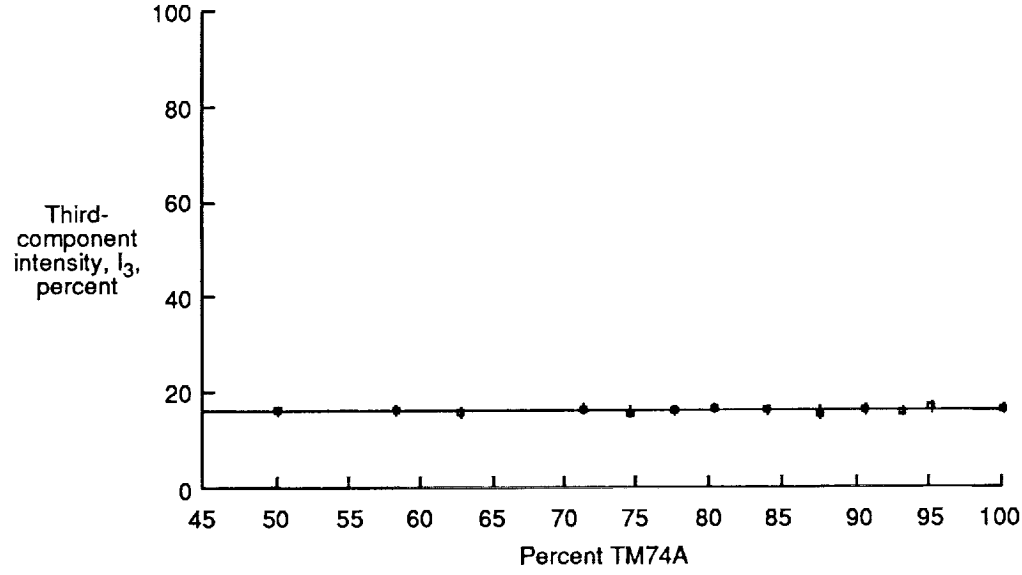

Figure 10. Third-component intensity versus percent of TM74A in mixture of TM74A and TM74A*.

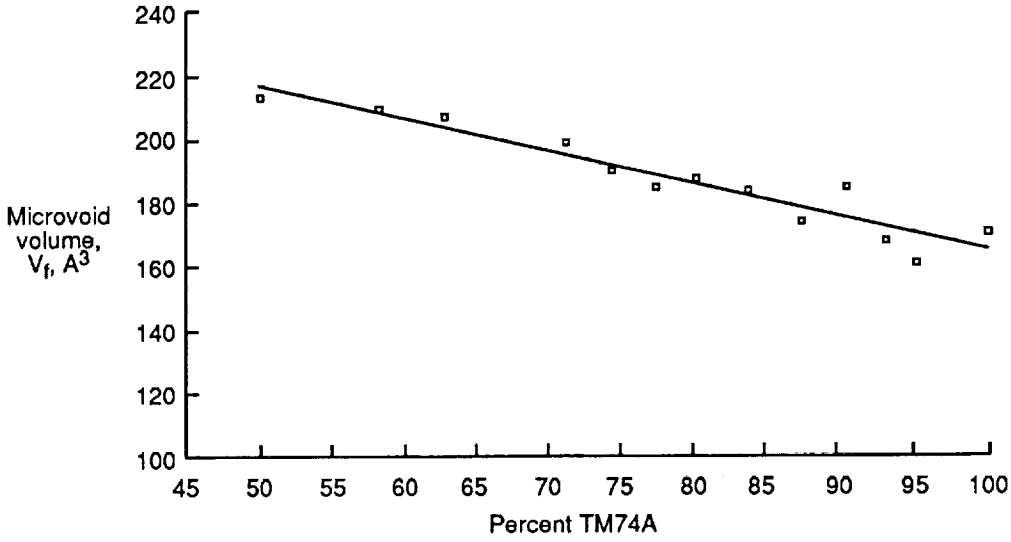

Figure 11. Microvoid volume versus percent of TM74A in mixture of TM74A and TM74A*.

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13. ABSTRACT *(Maximum 200 words)*

Positron lifetimes in the isotropic phases of chiral nematic liquid crystal formulations and their mixtures up to the racemic level have been measured. The lifetime spectra for all liquid crystal systems were analyzed into three components. Although the individual spectra in the left- and right-handed components are identical, their racemic mixtures exhibit much larger orthopositronium lifetimes; these larger lifetimes indicate the presence of larger microvoids. This result is consistent with the reportedly higher thermodynamic stability and color play range in the racemic mixtures of chiral nematic liquid crystals.

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