Kamlet-Taft Parameters in the Isotropic and Anisotropic Phases of the Nematic Liquid Crystal Mixture ML-0689: A Temperature-Dependent Approach

Bita Taheri[1], – Mohammad Sadegh Zakerhamidi[1]*
[1] Department of Photonics, Faculty of Physics, University of Tabriz, Tabriz, Iran

ABSTRACT

In light of the distinctive structural characteristics, liquid crystals are crucial to science and technology. Determining the solvent polarity characteristics of liquid crystals is critical for increasing their performance. In the present study, a dye-based spectroscopic approach for a mixed nematic liquid crystal was employed to calculate the Kamlet–Taft parameters. The results reveal that the anisotropic environment of the liquid crystal impacts the photophysical behaviour of solute molecules; in the nematic phase, changes in variables are gradual, however in the pretransitional zone, a quick and dramatic reduction is apparent. These outcomes emphasize the importance of examining solvent polarity factors at various temperatures to better understand molecular interactions in liquid crystal.

***Keywords**: ML-0689, Dye, Kamlet–Taft, Anisotropy, Transition temperature.*

1. *INTRODUCTION*

Anisotropy is a basic property found in liquid crystals, deriving from the lacking orientational order of its component molecules. This anisotropy gives birth to a spectrum of unique physical features, including as direction-dependent optical behaviour, dielectric response, and molecular mobility. As a result, liquid crystals play a crucial role in several optical, industrial, and therapeutic applications, where their sensitivity to external fields and their adjustable structural organization are particularly useful [1].

Liquid crystals' interactions with dissolved solute molecules are largely determined by the polarity of the solvent environment in addition to their structural anisotropy. Dipole–dipole effects, hydrogen bonding, and polarizability are examples of intermolecular interactions that are directly impacted by solvent polarity and have an impact on the photophysical behaviour of solute molecules. In order to explain solvatochromic shifts, fluorescence behaviour, and excited-state processes taking place inside liquid-crystal media, it is necessary to determine the polarity properties of an anisotropic solvent environment. [2–4].

Among the several techniques devised to quantify solvent polarity, the multiparameter Kamlet–Taft solvatochromic scale is regarded the most thorough and broadly applicable. This model isolates and evaluates the contributions of hydrogen-bond donating ability (HBD), hydrogen-bond accepting ability (HBA), and dipolarity/polarizability of the medium. The Kamlet–Taft equation, displayed in Eq. (1), describes the solvatochromic reaction of a probe molecule.

$$\nu = \nu_0 + a\alpha + b\beta + s\pi^* \qquad (1)$$

In this statement,

ν_0 is the reference transition frequency in the absence of solvent effects,
α signifies the solvent's hydrogen-bond donating acidity (HBD),
β represents its hydrogen-bond accepting basicity (HBA),
where π^* represents the solvent environment's dipolarity or polarizability.

The coefficients a, b, and s show the sensitivity of the solvatochromic probe to each of these interaction factors. Because this scale differentiates between specific and nonspecific solute–solvent interactions, it provides a valuable tool for assessing solvent polarity in anisotropic systems such as liquid crystals, where directional ordering contributes extra complexity into solvation dynamics [5].

The absorption maxima of a solvatochromic dye is determined in a range of solvents with various physicochemical characteristics in order to ascertain the polarity descriptors of a solvent system. Since these dyes' electronic transitions are so sensitive to environmental changes, they show observable spectrum alterations. Variations in the apparent wavelength (or wavenumber) indicate changes in polarity, hydrogen-bond donating or accepting capacities, and the general electrical nature of the medium. The Kamlet–Taft multiparameter equation may be used to analyze these spectrum shifts in order to identify and measure the distinct contributions of α (acidity of HBD), β (basic HBA), and π(dipolarity/polarizability), so offering a complete image of the solvent's polarity profile [5,6]. In this research, this solvatochromic technique was employed to evaluate the Kamlet–Taft characteristics of a nematic liquid-crystal mixture whose specific molecular composition was not entirely known. Because the solvation environment in liquid crystals varies greatly with phase structure, measurements were undertaken throughout various distinct sections of the phase sequence. These included the isotropic phase, when molecule orientations are random; the pretransitional zone along the isotropic–nematic boundary, where short-range orientational correlations arise; and the nematic phase, defined by long-range orientational ordering. By capturing absorption spectra across a wide temperature range, it was possible to gain understanding of how temperature variations affect solute–solvent interactions and change the medium's polarity. Since even small changes in molecular order can affect hydrogen-bonding interactions, local polarizability, and overall solvation dynamics within the anisotropic phase, such temperature-dependent solvatochromic analysis is particularly helpful for liquid-crystal systems [7–9].*

2. *EXPRIMENTAL SECTION*

2.1 Materials

Coumarin 504 and DRII (Figure 1), the dyes utilized in this investigation, were acquired as follows: Coumarin 504 was acquired from Sigma-Aldrich, whereas DRII was produced at the laboratory of the Department of Applied Physics at the University of Tabriz. Furthermore, 4-nitroaniline derivatives, including ethyl-4-nitroaniline, were first taken into consideration; nevertheless, DRII was employed as a suitable substitute because of their poor solubility in the UV area and incompatibility with the nematic liquid-crystal media. Moreover, as the Reichardt dye was insoluble, Coumarin 504 was utilized in this work. A nematic liquid-crystal mixture (ML–0688, Δε = 13.1) with positive dielectric anisotropy was used for the tests.

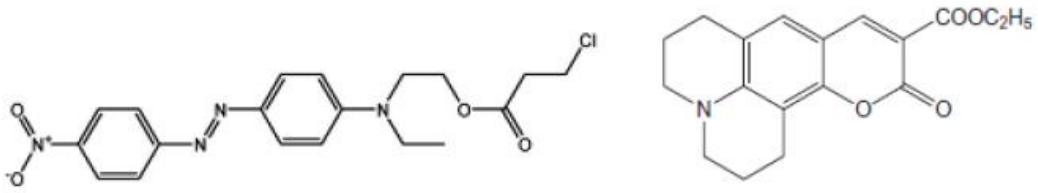


Fig. 1. *Chemical structures of the Coumarin 405 and DRII dyes.*

The anisotropic solvent environments used in this study are listed in Table 1.

Table 1. *Names and specifications of the anisotropic solvents used*

Liquid crystal	*TC / °C*	*Δε*	*Δn*
ML-0689	*77.1*	*13.1*	*0.63*

2.2 Absorption and emission spectroscopy

A double-beam Shimadzu UV-2450 UV-Visible spectrophotometer was utilized to collect absorption spectra. For spectroscopic studies quartz cells measuring (5 × 1 × 0.2 cm) were employed for research in the liquid crystal medium.

2.3 Estimation of polarity parameters

The maximum absorption wavelengths of the dyes in different solvents were determined to calculate the Kamlet–Taft polarity parameters. ET(30) was used to determine the hydrogen-bond donating ability (α), and (DRII) was used to determine π and β. Because coumarin 504 is sensitive to both specific and nonspecific solute-solvent interactions, it was used as the probe for the remaining parameters. The Kamlet-Taft values for each solvent were extracted by carefully analyzing the measured absorption maxima using the equations in Eqs. (2)–(9). This process offers a methodical and trustworthy way to measure solvent polarity, enabling the separation and comparison of the distinct contributions of hydrogen bonding and dipolarity/ polarizability in various solvent environments [10-12].*

$$\pi^* = \frac{\nu_{(\text{N,N-dimethyl-4-nitroaniline})} - 28.18}{-3.52} \qquad (2)$$

$$\nu_{(\text{N,N-dimethyl-4-nitroaniline})} = 1.1965\,\nu_{(\text{DRII})} + 594.39 \quad R = 0.98 \qquad (3)$$

$$\beta = \frac{0.9841\nu_{(\text{N,N-dimethyl-4-nitroaniline})} - \nu_{(4-nitroanilin)} + 3.49}{2.759} \qquad (4)$$

$$\nu_{(4-nitroaniline)} = 1.6897\nu_{(DR2)} + -8402.4 = 0.95 \qquad (5)$$

$$\alpha = \frac{E_T(30) - 14.6\pi^* - 30.31}{16.5} \qquad (6)$$

$$E_T(30) = \frac{28591.5}{\lambda_{\max(\text{Reichardt}-betaine-dye)}} \qquad (7)$$

$$E_T^N = \frac{E_T(30)_{Solvent} - 30.7}{32.4} \qquad (8)$$

$$v_{\text{Re}ichardt-betaine-dye} = -7{,}48v + 188778.00, R^2 = 0.99 \qquad (9)$$

3. *RESULTS AND DISCUSSION*

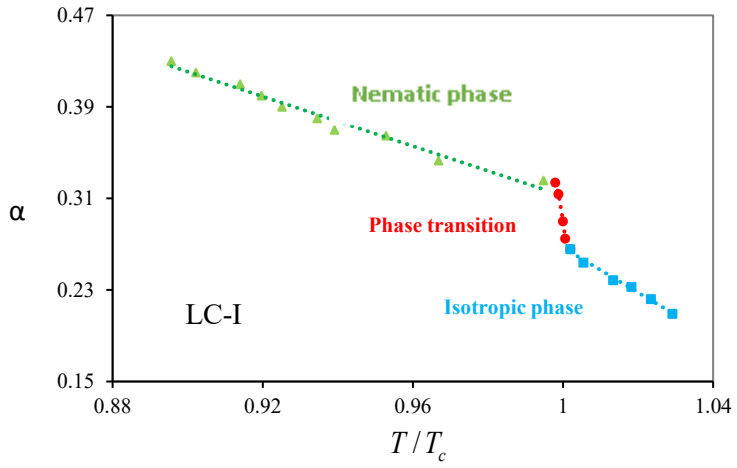
The maximum absorption wavelengths of DRII and Coumarin 504 in the nematic liquid crystal were utilized to compute the Kamlet–Taft solvent polarity parameters. Table 2 provides a summary of the corresponding values derived from these dyes' solvatochromic absorption spectra.

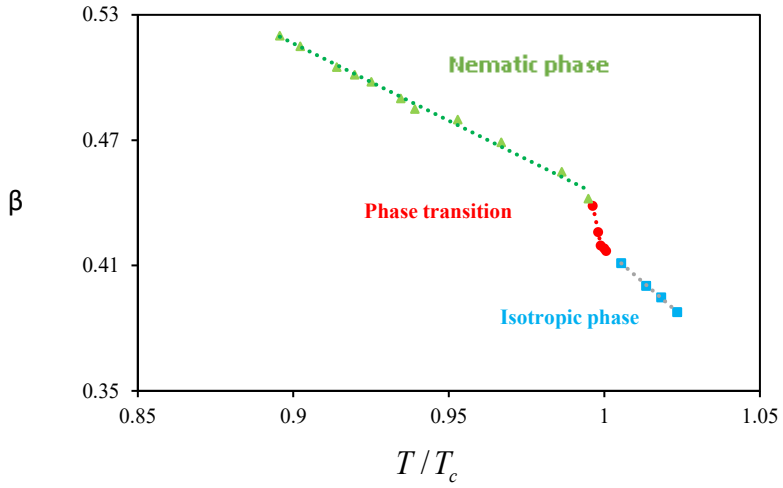
Table 2. *Kamlet–Taft Solvent Polarity Parameters of the Nematic Liquid Crystal at Room Temperature*

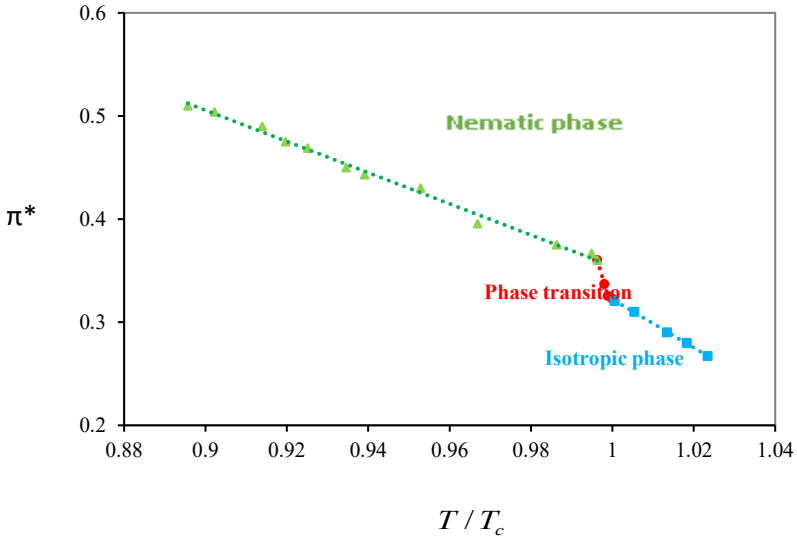
Liquid crystal	π^*	β	α	$E_T(30)$	E_T^N
ML-0689	*0.55*	*0.54*	*0.19*	*41.1*	*0.33*

As predicted, the nematic liquid crystal displays greater dielectric constant, β, and π values compared to conventional solvents. The comparatively high values of these characteristics show that the medium is extremely polar, indicating strong interactions between the liquid crystal molecules and polar solute molecules, even if the particular molecular structure of this liquid crystal is not fully described. Analysis of the Kamlet–Taft characteristics further indicates that this liquid crystal includes many hydrogen-bond-accepting groups (β), but its hydrogen-bond-donating ability (α) is comparably modest. These discoveries are consistent with the general behaviour of nematic liquid crystals, where directional ordering and anisotropic interactions contribute to higher dipolarity and hydrogen-bonding potential.*

In order to investigate how the solvent polarity of the liquid crystal changes with temperature, the maximum absorption wavelengths of the reference dyes were determined throughout a variety of temperatures in the ensuing tests. This method allowed for a thorough evaluation of the Kamlet–Taft polarity parameters' temperature dependence, offering insight into the relationships between solute–solvent interactions, phase transitions, and molecular order in the nematic medium.




0.53
0.47
0.41
0.35
β
Nematic phase
Phase transition
Isotropic phase
0.85
0.9
0.95
1
1.05
T/T_c


0.6
0.5
0.4
0.3
0.2
π*
Nematic phase
Phase transition
Isotropic phase
0.88
0.9
0.92
0.94
0.96
0.98
1
1.02
1.04
T/T_c

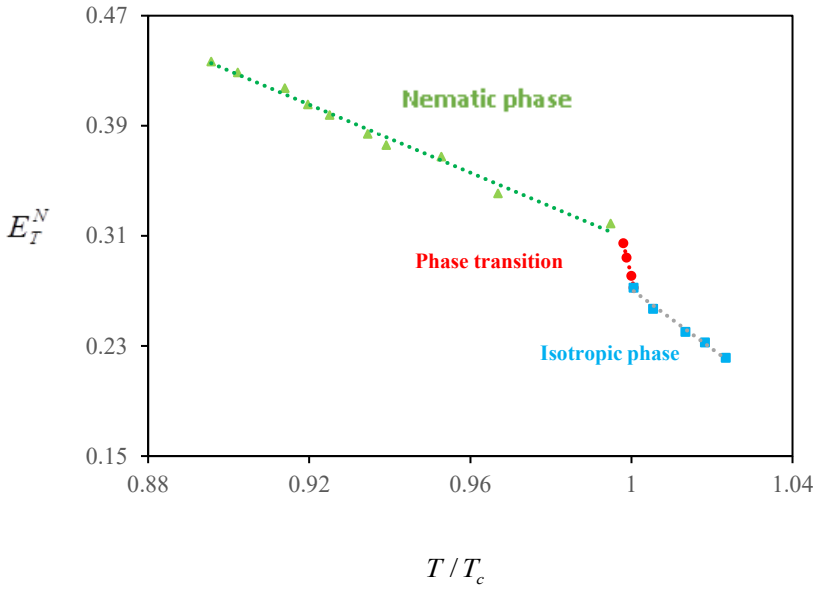


Fig. 2. *Effect of temperature variation on the Kamlet–Taft solvent polarity parameters of the ML–0689 liquid crystal.*

Figure 2 displays the influence of temperature on the Kamlet–Taft solvent polarity characteristics of MLC-0689. As the image indicates, the overall solvent polarity diminishes with increasing temperature, indicating the degradation of orientational order and the weakening of intermolecular interactions at greater thermal energy. The comparatively little change in polarity during the nematic (anisotropic) phase suggests that the solvation environment is somewhat stabilized by the ordered molecular structure. In contrast, in the pretransitional region just before the transition from nematic to isotropic phase the solvent polarity characteristics decrease dramatically, with a substantially steeper slope. This shows that the pretransitional variations severely disturb molecular alignment and solute–solvent interactions, resulting in fast shifts in the polarity experienced by the solute. The solvent polarity steadily decreases with temperature in the isotropic phase, but more slowly than in the pretransitional zone. The lack of long-range molecular organization results in a more uniform but less strongly interacting medium, even if the polarity is still slightly greater than in the nematic phase. In the end, these findings show that the liquid crystal's phase and temperature have a significant impact on its Kamlet–Taft solvent polarity characteristics. The results show the susceptibility of liquid-crystal media to temperature and structural differences, which must be addressed when interpreting photophysical behaviour or developing applications requiring solute–solvent interactions in such anisotropic settings.

CONCLUSION

The findings show that there is a significant contact between the liquid crystal molecules and the solvatochromic dyes, with dipole–dipole interactions being primarily responsible for stabilizing the solute in the anisotropic media. The unusually high values of β and π are consistent with this discovery, showing the polar character of the liquid crystal environment. These results imply that the liquid crystal molecules have large molecular dipoles and hydrogen-bond-accepting groups, which enable strong electrostatic interactions with polar solutes. Furthermore, these interactions are strengthened by the directional ordering in the nematic phase and the molecules' intrinsic polarity, which causes the dyes to exhibit noticeable solvatochromic changes. comprehending photophysical behaviour and how molecular structure influences solvation and polarity-dependent processes in liquid crystals requires a knowledge of such intense solute–solvent interactions.*

REFERENCES

[1] M. S. Zakerhamidi, H. Tajjali, M. Moghaddam, M. Jassas & R. Hosseini Nasab, "Spectrochemical Study," Spectrochimica Acta Part A, 2010, 77, 337–341.

[2] J. L. Atwood, J. W. Steed (Eds.), Encyclopedia of Supramolecular Chemistry, CRC Press, 2004 – section on solvatochromism and solvent effects.

[3] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, 4th ed., Wiley-VCH, 2011.

[4] C. Reichardt & T. Welton, "Solvatochromism," Chemical Reviews, 2011, 111, 123–150.

[5] M. J. Kamlet, J. L. M. Abboud, M. H. Abraham & R. W. Taft, "Linear Solvation Energy Relationships. 23. A Comprehensive Collection of the Solvatochromic Parameters π, α, and β," Journal of Organic Chemistry, 1983, 48, 2877–2885.*

[6] C. Reichardt, "Solvatochromic Dyes as Solvent Polarity Indicators," Chemical Reviews, 1994, 94, 2319–2358.

[7] S. Urban & P. K. Dąbrowski, "Pretransitional and Critical Phenomena in Liquid Crystals," Reports on Progress in Physics, 2014, 77, 016601.

[8] P. K. Mandal & K. Bhattacharyya, "Solvation Dynamics in Liquid Crystals," The Journal of Physical Chemistry A, 2005, 109, 5698–5702.

[9] T. Kato, "Self-Assembly of Liquid-Crystalline Functional Materials," Nature Chemistry, 2010, 2, 587–594.

[10] B. Taheri, M. S. Zakerhamidi, A. N. Shamkhali, R. Kian & A. Amiri Sadeghan, "Solvent polarity effect on photophysical properties of some aromatic azo dyes with focus on tautomeric and toxicity competition," Scientific Reports, 2025, 15(1), Article 15716.

[11] R. Kian, M. S. Zakerhamidi, A. Ranjkesh, A. N. Shamkhali, et al., "Investigation of the spectroscopic features along with the media polarity effect in some symmetrical disc-shaped liquid crystals," Journal of Molecular Liquids, 2020, 309, 113226.

[12] B. Taheri, M. S. Zakerhamidi, R. Kian, A. Amiri Sadeghan, "Solvent-Dependent Photophysical Behavior of Xanthene Dyes and Their Intrinsic Polarity Descriptor: A Study of Erythrosine B and Rose Bengal," Journal of Molecular Structure, 2025, 1349, 143840.