

ISOMERIC DISTRIBUTION OF FLUORESCENT LASER DYE DCM IN METHANOL AND IN GAS PHASE: AN ION MOBILITY MASS SPECTROMETRIC STUDY IN COMBINATION WITH HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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The isomeric distribution of a popular fluorescent laser dye DCM (4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran) has been investigated both in methanol solution and gas phase using the multi-dispersive experimental technique involving Ion Mobility Mass Spectrometry (IMMS) and High Performance Liquid Chromatography (HPLC). There could be four rotameric forms, trans1, trans2, cis1, and cis2. Chromatographic separation of the isomers in methanol solution shows two distinctly separated peaks at retention times of 3.73 (peak-I) and 3.87 (peak-II) minutes. In the case of optical probing, the former peak appears much weaker compared to the latter when probed at the absorption maximum of the dye at 467 nm. On the other hand, in mass spectrometric probing corresponding to the molecular mass (DCMH^+), peak-II is found to be nearly twice as intense as peak-I. The ion mobility measurements have been performed with the two LC separated solution fractions and in each case, three peaks, A, B and C, are observed, whereby the collision cross-section (CCS) values corresponding to these peaks are found to be 174, 185 and 197 \AA^2 , respectively. Interestingly, the relative intensities of these three peaks in the two IM spectra appear in opposite sequences. The minimum energy geometries of the neutral and protonated isomers have been computed by electronic structure theory method and the CCS values of the protonated isomers have been calculated using the MOBCAL program. The analysis reveals that the LC peak-I is associated with the cis2 isomer, whereas the other three isomers contribute collectively to peak-II. By simulating the electronic absorption spectral profiles of the isomers, we have proposed that the distributions of the trans1, trans2, cis1, and cis2 isomers are 33.5, 61.5, 2.0 and 3.0%, respectively, in the solution phase. The IM spectral features also indicate occurrences of isomeric inter-conversions during the ESI process. The collision-induced dissociation of the DCMH^+ ions corresponding to the LC separated solution fractions reveals that the fragmentation behavior is also isomer dependent.