Dispersion of Nicotine Circular Birefringence

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The dispersion of nicotine's circular birefringence in the visible range was determined from the channeled spectrum and verified using a polarimeter standardized in yellow light of a Natrium lamp. The obtained results are in agreement with the data from literature.

Keywords: nicotine; optical activity; dispersion of the circular birefringence; channeled spectrum

Optically active materials have found widespread applicability in various fields, such as pharmaceutical industry, optical communications and detectors [1-3]. In the last case, the main idea is that polarized light interacting with chiral compounds can be used to detect and recognize biological and chemical materials. Among the substances that have the ability to rotate the plane of polarization of light, nicotine was widely studied since it is often found in tobacco products, it is used as a pesticide or as an experimental drug to help in smoking cessation therapy [4]. There are two enantiomeric forms for this compound, namely (S)-(–)-nicotine and (R)-(+)-nicotine. The first enantiomer, also known as 3-(1-methyl-2-pyrrolidinyl) pyridine, is an alkaloid found in tobacco under the form of an oily liquid, which is widely used in applications [4]. The second enantiomer is less common, but it exhibits an interesting biological activity [4].

Fundamental research on optical activity of nicotine started in 1893 by Landolt [5], which reported a specific rotation of -161.55° at 589 nm, which slightly differs from that published in 1918 by Jephcott [6], *i.e.* - 168.5°. The explanation for this discrepancy could reside in the fact that specific rotation is sensitive to the method used to purify nicotine [5]. When the samples are processed by distillation under hydrogen, specific rotation varies in the interval of -161° to -165° [7]. When nicotine is purified through vacuum distillation the specific rotation is close to that reported by Jephcott [6]. This was also confirmed by Norton et al. [8], which, by using the same processing method, achieved a specific rotation of - 168.9°. Optical activity of nicotine was also analyzed in systems that are more complex. For instance, Tomita et al. [9] evaluated the impact of hydrogen chloride on the optical rotation of nicotine. The protonation of nicotine affects in a similar manner the rotatory dispersion of samples in 95% alcohol and in water. The circular dichroism curves present a positive Cotton effect at 245 nm and a negative Cotton effect at about 268 nm as a result of the π - π ^{*} transition in the pyridine group. Optical rotation is enhanced as the hydrogen chloride concentration reaches a mole ratio of 1, afterwards decreases by further addition of hydrogen chloride. This behavior was found to be analogous to that of nicotine-Lewis acid systems [9].

Michailov and Baldjieva [10] evaluated the optical activity of poly (methacrylic acid) (PMMA) salts with nicotine in aqueous solution. They prepared solutions of

various concentrations of nicotine salts of PMMA, nicotine salts of pivalic acid, and aqueous solutions of nicotine. Optical rotation measured at 436 nm, 546 nm and 589 nm showed no linear relationship with solution concentration. The specific rotation of aqueous nicotine solutions without electrolyte has negative values, while in the presence of salts it becomes positive. The optical activity of the nicotine salt samples estimated on the basis of the specific rotations of nicotine cation and nicotine base molecule is quite distinct from the measured one. The result was explained by considering a higher specific rotation of the associated nicotine cations [10]. After a few years, Michailov and Baldjieva [11] continued their studies by examining the temperature effect on optical activity of nicotine salts of PMMA solutions. Their investigation highlighted a nonlinear temperature dependence of the optical activity. This aspect indicated important modifications in structure and proteolytic equilibrium of nicotine-based solutions [11]. Armstrong and co-workers [4] have studied the enantiomeric composition of nicotine in tobacco, medicinal or commercial reagents. They found that the content of the minor enantiomeric component, (R)-(+)nicotine varied from $\sim 0.1\%$ to $\sim 1.2\%$ of the nicotine in all systems. Clayton et al [12] analyzed the spectral characteristics of nicotine in UV region. Besides the ð-ð* transition at 263 nm and $n-\pi^*$ transition at 240 nm, they revealed the existence of four previously unobserved electronic transitions between 215 and 180 nm.

The aim of this study was to estimate the visible circular birefringence and its dispersion in the case of nicotine, using channeled spectrum of pure nicotine kept in a special tube, due to its appreciably evaporation in air at room temperature.

As one of the 7000 compounds in tobacco smoke, nicotine has the capacity to penetrate all tissues in the body and bind to nicotinic-acetylcholine receptor [13]. Usually, nicotine is associated with lung cancer and continuous tobacco use during cancer treatment is associated with poor therapeutic results [14,15].

Experimental part

Pure nicotine (\geq 99%) was purchased from Sigma-Aldrich (now Merck).

The circular birefringence and its dispersion are measured from the channeled spectrum [16-18] recorded at a spectrophotometer Specord UV Vis Carl Zeiss Jena

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with data acquisition. The experimental set-up designed [16,17] for circular birefringence dispersion consists by two devices: one is introduced in the measure beam and has two crossed polarizing filters with the tube containing the optically active substance between them [18] and the second one consists from two polarizing filters with the transmission direction in parallel for compensation reasons. This method can be applied for both transparent solutions [18,19] and transparent optically active crystalline layers [17, 20-22].

Theoretical background

Optical activity is the phenomenon of rotation of electric field around the propagation direction of polarized light due to the chirality of the molecules composing the sample. Theory of optical activity considers the linearly polarized radiations decomposed in two circularly polarized, to left and to right, components that propagate with different velocities in the transparent medium. At the exit from the optical active substance, different components of light are rotated with different angles relative to the direction of polarization of the incident radiation.

The transmission factor $T(\lambda)$ of the device introduced in the measure beam depends on the circular birefringence Δn , on its dispersion, δ , and on the thickness *L* of the optical active sample, as it follows [17]:

$$T(\lambda) = \frac{\varphi_e}{\varphi_i} = \sin^2 \frac{\pi}{\lambda} \Delta n_c L , \qquad (1)$$

In relation (1), λ is the wavelength of the radiation in vacuum; ϕ_{e} and ϕ_{i} are the flux densities in the emergent and the incident beams, respectively.

When the conditions for the maximum and minimum of the transmission factor are written [17, 21] for two neighboring minima (of order k + 1 and k, situated at wavelengths λ_{k+1} and λ_k with $\lambda_{k+1} \leq \lambda_k$, respectively) and for the maximum of order k + 1/2 between them, the solutions of the obtained equations are [17,18]:

$$\Delta n_{\varepsilon} = \frac{\lambda_{k+\frac{1}{2}}(\lambda_{k+1} - \lambda_{k})}{2L\left(2\lambda_{k+\frac{1}{2}} - \lambda_{k+1} - \lambda_{k}\right)}$$
(2)

and

$$\mathcal{S} = \frac{\lambda_{k+\frac{1}{2}}(\lambda_{k+1} + \lambda_k) - 2\lambda_k\lambda_{k+1}}{2L\left(2\lambda_{k+\frac{1}{2}} - \lambda_{k+1} - \lambda_k\right)}.$$
(3)

The measurements based on the channeled spectrum have the advantage that gives information regarding the circular birefringence and its dispersion relative to all light components from visible range.

The wavelengths of the two minima and the maximum between them or of two maxima and the minimum between them and knowledge about the thickness of the layer are necessary for estimating the circular birefringence and its dispersion [17,18].

Results and discussions

Experiments made with a simple polarimeter show the negative (to left rotation) character of the nicotine optical activity. For $\lambda = 589.3$ nm, for which the polarimeter was standardized, the angle of rotation determined by a nicotine layer of L = 10 cm was - 161 degrees.

The layer of pure nicotine rotates the polarization plane of each component of the visible light with different angles and the results recorded at spectrophotometer is an channeled spectrum (Fig. 1) with minima corresponding to the radiations with rotation angles an multiple of π radians, as relation (1) indicates.



Using relations (2) and (3), the circular birefringence Δn_c (Fig. 2) and its dispersion δ (Fig. 3), are obtained for the visible range.



Fig. 2. Circular birefringence of nicotine in the visible range



Fig. 3. Circular birefringence dispersion of nicotine in the visible range

The specific rotation vs. light wavelength obtained from the analysis of the channeled spectrum of pure nicotine is plotted in figure 4.

The module of the specific rotation decreases at high wavelengths as it results from Fig. 4. The specific rotation is dependent on the concentration of nicotine in an organic solvent with hydroxy character, due to the specific interactions possible to act by formation of nicotine



Fig. 4. Specific rotation of visible components of radiations

complexes through hydrogen bonds. Previous studies showed this dependence. Our determination emphasized a non-linear dependence of the specific rotation as function of nicotine concentration in water solutions. This dependence can be used to determine the nicotine concentration especially in the linear part of the dependence.

Conclusions

Pure nicotine is used to determine the channeled spectrum and to estimate the circular birefringence and its dispersion in the visible range. Nicotine is characterized by negative optical activity.

Based on the concentration dependence of the specific rotation in nicotine aqueous solutions, one can determine the unknown nicotine concentration in water.

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