

Effects of Non-Equilibrium Plasma Processing on Solutions of D-, L-Isomers

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ABSTRACT

This work is devoted to the study of the possibility of violating one of the basic provisions of chemical thermodynamics in a strongly non-equilibrium plasma-chemical system. Particular attention is paid to the fact that “living” biomaterials are characterized by both the arrangement of chiral components and the course of chemical transformations in organic chemistry under quasi-equilibrium conditions. In view of this, the features of the plasma effect on aqueous solutions of D fructose, D glucose, D tartaric acid and ethanol solutions of D fructose and L proline are considered, which is associated with the introduction of energy by the plasma flow sufficient for significant destruction of organic molecules. The non-equilibrium of the plasma-chemical system provides not only a significant energy-mass exchange with the environment, but also the absence of equivalence in the directions of motion of reagent particles, which is realized by the gas dynamics of the rotating gas flow in the system.

Determination of such physicochemical properties of solutions as optical activity of solutions, adsorption spectra in UV and IR ranges, Raman scattering spectra and NMR spectroscopy on protons and ¹³C nuclei was carried out before and after their plasma activation. Optical activity was determined using a laser modulation polarimeter. Transmittance in the UV range -200 - 400 nm was determined using a spectrometer with a CCD detector (Solar TH). Transmittance in the IR range (500 - 4000 cm⁻¹) was determined using a Fourier spectrometer. Raman spectra (70 - 3600 cm⁻¹) were obtained in quasi-backscattering geometry using a Horiba Jobin-Yvon T64000 triple spectrometer with an integrated micro-Raman scattering setup - an Olympus BX-41 microscope and a Peltier-cooled CCD detector.

It is shown that the spectral characteristics of the studied solutions of optically active isomers change significantly after plasma treatment: the nature of the change is influenced by both the direction of rotation of the gas flow in the system and the nature of the optical activity of the dissolved initial isomer. The change in the throughput of the solutions in the UV range indicates a significant destruction of the initial hydrocarbon reagent. Spectroscopic studies (in the UV and IR ranges, NMR-¹³C) of L-proline in C₂H₅OH solutions activated by the plasma of an immersed rotating sliding discharge, Raman scattering of solid-phase precipitates formed after solvent evaporation revealed a significant influence of the direction of rotation of the gas flow in the plasma-liquid system on the kinetics of physicochemical processes in it. The optical activity of solutions during the first hours after treatment changes chaotically, but its stabilization time does not exceed 1 day for solutions of glucose, fructose, proline and tartaric acid.

The main conclusion from the study of solutions after plasma activation in an open non-equilibrium plasma-liquid system, which has significant parameter gradients and does not have a uniform probability in the directions of forced rotation of reagent particles using solutions of chemically pure, optically active reagents, is that plasma activation enables both destructive processes and a significant change in the optical activity of solutions. The change in the optical activity of solutions of polar chiral substances (glucose and fructose) after plasma activation noticeably depends on the direction of forced rotation of reagent particles. The influence of the direction of forced rotation of reagent particles on the change in the optical activity of solutions of non-polar chiral reagents (proline and tartaric acid) was practically absent.

Keywords: Solutions Of Polar and Non-Polar Chiral Substances, Plasma Activation of Solutions, Optical Activity of Solutions, Plasma-Liquid System, Rotating Gas Discharge

Introduction

In today's world, many industries, including medicine and cosmetology, use technologies based on the interaction of high-energy particles with biomaterials. The energy levels of these particles are comparable to or exceed the energies of chemical and physical bonds in biomaterial atoms and molecules. These particles include photons in the UV optical range, used in cosmetology, and charged and neutral particles with kinetic and internal energies ranging from a few to tens of electron volts, used in plasma medicine, as well as from a few to tens of kiloelectron volts, used in medical applications.

In physics, this interaction of beams with matter is characterized as an introduction of energy into a system, leading to the system transitioning from an equilibrium state to a non-equilibrium state. In such a state, the rates of dissociative processes exceed those of the reverse associative processes. After the external influence ceases, the excited system undergoes relaxation, transitioning back from a non-equilibrium state to an equilibrium state where the rates of dissociative processes decrease, and the rates of associative processes increase.

Thus, physical actions allow for maintaining non-equilibrium conditions for physicochemical processes within specific spatial regions or time frames. In such conditions it is essential that processes can only be adequately described using kinetic approach, particularly relevant to the fields of plasma and radiation chemistry.

Our research examines several fundamental aspects of plasma flow interacting with biomaterials, taking into account the established principles of organic chemistry. Special attention is given to the features of "living" biomaterials that include chiral components, which undergo chemical transformations under quasi-equilibrium conditions. With this in mind, we studied the specific effects of plasma on aqueous solutions of D-fructose, D-glucose, D-tartaric acid, and on solutions of D-fructose and L-proline in ethanol, introducing energy levels sufficient to cause significant destruction of organic molecules. This study aims to explore the potential of plasma technology to influence the structural and chemical properties of organic compounds in solutions.

There exists a well-known universal rule in organic chemistry: "Synthesis of chiral compounds from achiral reagents always leads to racemic modification" [1].

This principle is grounded in the laws of thermodynamics, where both L- and D-forms of a substance possess identical free energy (G), making the free energy difference (ΔG) between them zero. The chemical equilibrium constant (K) is a value that represents the interdependence between the concentrations of substances in a system reacting according to an equation that reflects the stoichiometry and functional membership of the components when chemical equilibrium is reached. The equilibrium constant for any reaction (K) is the equilibrium ratio of the concentration of products to the reactant. The reaction between these two

elements at any temperature (T, K) is represented by the standard formula:

$$K = \exp (-\Delta G/RT), \quad (1)$$

where $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ is the absolute gas constant - a fundamental physical constant. For the reaction of changing "left" amino acids to "right" ($L \rightarrow D$) or back ($D \rightarrow L$), $\Delta G = 0$ so that $K = 1$.

Therefore, the reaction reaches equilibrium when the concentration of "left" and "right" forms of molecules is the same, meaning a racemate is created. This explains the above rule of organic chemistry [2].

In view of the above, it is not possible to expect a violation of this rule under the conditions of a weak disturbance of the system equilibrium during chemical transformations under quasi-equilibrium conditions, which is characteristic of traditional organic chemistry. At the same time, for very unbalanced systems, the question of a possible violation of this rule remains open and practically unexplored. Such non-equilibrium in chemical processes always occurs in open systems and in almost all cases when, in addition to purely thermal excitation, there is an influence of physical fields (external and internal) on the speed and characteristic features (selectivity!) of chemical reactions [3].

This paper is devoted to researching the possibility of violation of one of the basic provisions of chemical thermodynamics in a strongly non-equilibrium plasma-chemical system. Special attention is given to the fact that "living" biomaterials are characterized not only by their composition of chiral components but also by the course of chemical transformations in organic chemistry under quasi-equilibrium conditions. In light of this, the peculiarities of plasma effects on aqueous solutions of D-fructose, D-glucose, D-tartaric acid, and solutions of D-fructose and L-proline in ethanol are considered, which involve the introduction of a plasma stream of energy sufficient for significant destruction of organic molecules. The non-equilibrium nature of the system not only ensures substantial energy-mass exchange with the environment but also the absence of equiprobability in the directions of movement of reactant particles, realized by the gas dynamics of the rotating gas flow in the system.

Previously, we have synthesized an optically active substance in a similar experimental plasma-chemical system using only optically inactive source substances H_2O , CO_2 , NH_3 , $\text{C}_2\text{H}_5\text{OH}$ [4].

The main provisions of the physical mechanism of the appearance of optical activity founded on the basic provisions of the physics of elementary processes in those experiments were presented in the papers [5,6].

Materials and Methods

Plasma activation of chemical transformations was carried out in an experimental system with a rotating gliding discharge immersed in a liquid, which is presented in Figure 1 [4].

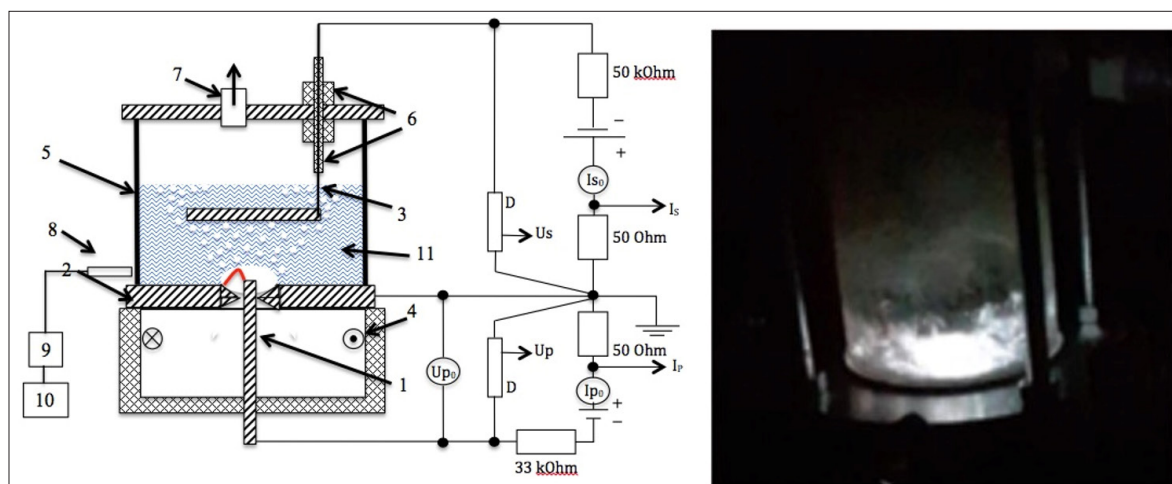


Figure 1: The experimental system with a rotating gliding discharge immersed in a liquid - (A): 1 - high-voltage primary discharge electrode; 2 - grounding electrode; 3 - high-voltage secondary discharge electrode; 4 - gas inlet; 5 - quartz cylinder; 6 - dielectric; 7 - gas outlet; 8 - optical fiber; 9 - spectrometer; 10 - PC; 11 - liquid. Photo of the rotating gliding discharge immersed in a liquid - (B).

The plasma generator consists of an upper flange (*cathode*), a central electrode (*anode*) and a dielectric chamber with holes for tangential supply of the working gas. The central part of the cathode has a conical shape with a hole in the center. The diameter of the hole is 3 mm. A rotating gliding discharge is ignited between the cathode and the anode. The distance between the cathode and the anode is 1 mm. A quartz cylinder was placed on the cathode, into which the test solution was fed by a peristaltic pump (Vakarov). CO₂ was used as a working gas. The gas was fed into the dielectric chamber tangentially to the system axis, which led to spinning of the gas flow in the specified direction. The design of the chamber made it possible to change the gas flow spinning direction to the opposite. The outflow of gas through the central hole in the flange created a gas cavity in the lower part of the liquid layer, in which the electric discharge burned. The outflow of gas from the gas cavity into the liquid was observed in the form of bubbles which had not only an axial, but also an azimuthal component of velocity in the rotating gas flow. The discharge current channel and the liquid layer also rotated around the system axis. The CO₂ flow was 10 l/min. The gas outlet from the system was connected to a return cooler, after which the gas was exhausted into the ventilation system.

The gas was fed tangentially to the system axis. CO₂ was used as a working gas. Depending on the gas supply direction, the discharge burned in the gas flow rotating clockwise or counterclockwise. The electric field of the gas discharge was always directed perpendicular to the azimuthal component of the gas flow velocity.

Gas discharge plasma activation was carried out for aqueous solutions of 0.24 M D-glucose, 0.101 M D-fructose, 0.22 M D-tartaric acid and solutions in ethanol of 0.101 M D-fructose and 0.24 M L-proline. During plasma activation, the rotating gliding discharge current was equal to 100 mA, the CO₂ flow was 10 l/min. The treatment duration τ was chosen taking into account the possible evaporation of the solvent and, accordingly, the possible change in the solution concentration (<5%): $\tau \geq 20$ min for aqueous solutions, $\tau = 10$ min for solutions in ethanol.

The electric gas discharge was powered by a high-voltage direct current source (BP-100). The voltage drops across the discharge was measured using an ohmic voltage divider, the discharge current was determined by the voltage drop across the measuring resistor (50 Ω); both were connected to an oscilloscope (INSTRUSTAR-ISDS205A).

During the burning of the discharge, the emission spectrum of the gas-discharge plasma was measured in the range of 200-1000 nm using a spectrometer with a CCD detector (Solar TII).

Determination of such physico-chemical properties of solutions as optical activity of solutions, adsorption spectra in the UV and IR ranges, Raman scattering spectra and NMR spectroscopy on protons and ¹³C nuclei was carried out on AVANCE 400 (BRUCER, Germany) before and after their plasma activation.

Optical activity was determined using a laser modulation polarimeter [4].

Transmittance in the UV range 200 - 400 nm was measured by a spectrometer with a CCD detector (Solar TII). Transmittance in the IR range (500 - 4000 cm⁻¹) was determined using a Fourier spectrometer. Raman scattering spectra (70 - 3600 cm⁻¹) were obtained in quasi-backscattering geometry using a Horiba Jobin-Yvon T64000 triple spectrometer with an integrated micro Raman scattering setup - an Olympus BX-41 microscope and a Peltier-cooled CCD detector.

Results and Discussion

Optical activity of solutions: The optical activity of the solutions was determined by the difference in the angles of the light polarization plane after the passage of polarized light through quartz cuvettes 4 cm long filled with the investigated solution and distillate. The specific feature of these measurements for all solutions after plasma treatment was a large instability observed for several hours. Therefore, the actual determination of the optic activity was started after their daily settling in sealed plastic containers (100 cm³). The initial non-plasma-activated solution (~ 100 ml) was stored under the same conditions. For each measurement, 10 ml of the solution was taken, which was

disposed after determining the optical activity. The angular position of the polarization plane was determined by averaging 5 independent readings, while in the case of distillate, the average square deviation from the mean did not exceed 20". Similarly obtained time dependences of the optical activity of solutions of both initial (Plasma Off) and plasma-activated (Plasma On) gas discharges in a spinned flow in two modes in the direction of spinning clockwise (cw) and counterclockwise (ccw) are given for water solutions of chiral sugars with different directions of optical activity in Figures 2 and 3 and for tartaric acid, in Figure 4.

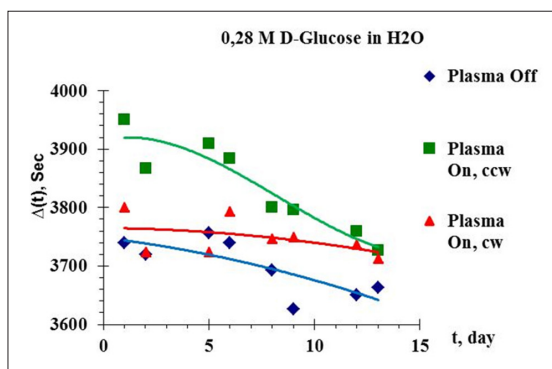


Figure 2: Time dependences of the optical activity value of a solution of 0.28 M D-Glucose in water, both initial (Plasma Off) and plasma-activated (Plasma On) in two modes in the direction of spinning of the CO₂ flow in the system: clockwise - cw and counterclockwise - ccw.

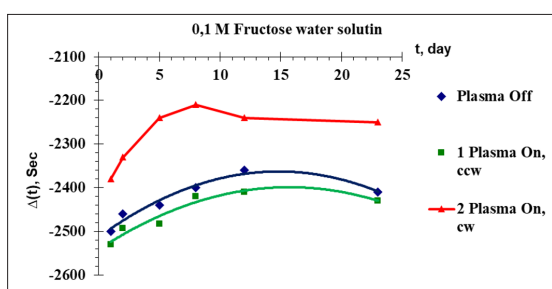


Figure 3: Time dependences of the optical activity value of a solution of 0.1 M Fructose in water, both initial (Plasma Off) and plasma-activated (Plasma On) in two modes in the direction of spinning of the CO₂ flow in the system: clockwise - cw and counterclockwise - ccw.

As can be seen from the obtained time dependences of optical activity in the case of sugars, a significant change in optical activity was observed after plasma activation of a gas discharge with a rotating plasma column. Moreover, a distinct dependence of the absolute change in optical activity on the gas flow rotation direction is clearly observed. In the case of an aqueous solution of tartaric acid, such changes are practically absent.

An important result is the comparison of the obtained time dependences of the optical activity of fructose solutions of the same molarity in different solvents: water (Figure 3) and ethyl alcohol (Figure 5), as well as tartaric acid in water and L-proline in ethyl alcohol (Figure 6).

On the one hand, the greatest change in the optical activity of the sugar (fructose) solution was observed in the same direction

of the gas flow spinning (cw) regardless of the solvent, but in the case of the solution in water, plasma activation led to a decrease in α , while in the case of the solution in ethyl alcohol, on the contrary, to an increase. For fructose solutions in the ccw plasma treatment mode, an increase in optical activity compared to the initial untreated solution is noticeable for both solvents, although the absolute change in α was greater for the solution in ethyl alcohol.

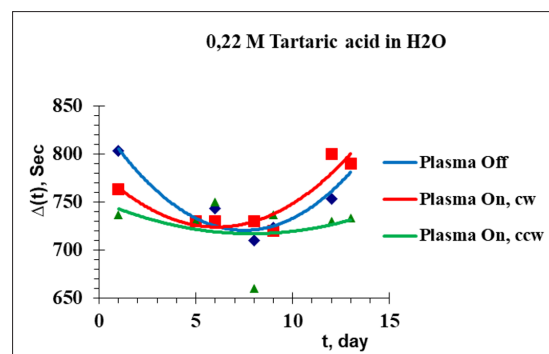


Figure 4: Time dependences of the optical activity value of a solution of 0.22 M Tartaric acid in water, both initial (Plasma Off) and plasma-activated (Plasma On) in two modes in the direction of spinning of the CO₂ flow in the system: clockwise - cw and counterclockwise - ccw.

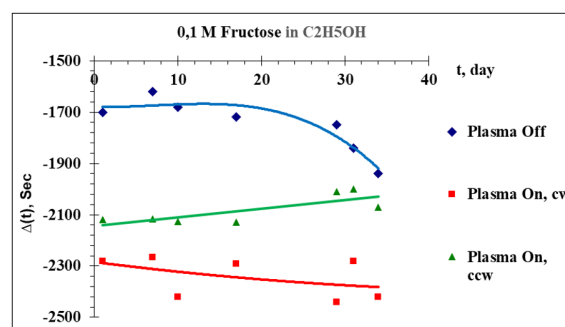


Figure 5: Time dependences of the optical activity of a solution of 0.1 M Fructose in ethanol, both initial (Plasma Off) and plasma-activated (Plasma On) in two modes of the direction of spinning of the CO₂ flow in the system: clockwise - cw and counterclockwise - ccw.

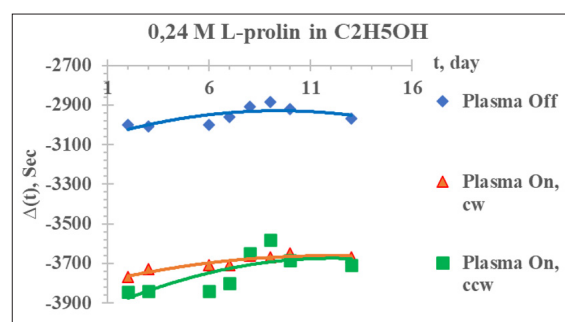


Figure 6: Time dependences of the optical activity of a solution of 0.24 M solutions of L-proline in ethanol, both initial (Plasma Off) and plasma-activated (Plasma On) in two modes in the direction of spinning of the CO₂ flow in the system: clockwise - cw and counterclockwise - ccw.

A comparison of changes in the optical activity of acid solutions after plasma activation (tartaric acid in water - Figure 5) and L-proline in ethyl alcohol (Figure 6) revealed, on the one hand, that the transition from a simple solvent (water) to an organic solvent leads to a significant increase in α , while the influence of the rotation direction in the plasma-liquid system due to the rotating CO₂ flow injection into the system is practically absent.

The main conclusion from the study of solutions after plasma activation in an open non-equilibrium plasma-liquid system, which has significant parameter gradients and does not have a uniform probability in the directions of forced rotation of reagent particles using solutions of chemically pure, optically active reagents, is that plasma activation enables both destructive processes and a significant change in the optical activity of solutions. The change in the optical activity of solutions of polar chiral substances (glucose and fructose) after plasma activation noticeably depends on the direction of forced rotation of reagent particles. The influence of the direction of forced rotation of reagent particles on the change in the optical activity of solutions of non-polar chiral reagents (proline and tartaric acid) was practically absent.

Adsorption properties of solutions in the UV ranges of light: The obtained dependences of the absorption coefficient k of the initial solutions of glucose, fructose in water and L-proline in alcohol and after their plasma activation are shown in Figures 7 - 9. The absorption coefficient was determined according to Bouguer's law

$$I(\lambda) = I_0(\lambda)e^{-k(\lambda)l}, \quad (2)$$

where $I(\lambda)$ is the light intensity after passing through the cuvette with the investigated solution, $I_0(\lambda)$ is the light intensity after passing through the cuvette filled with distillate, $l = 1$ cm is the optical path of light in the solution.

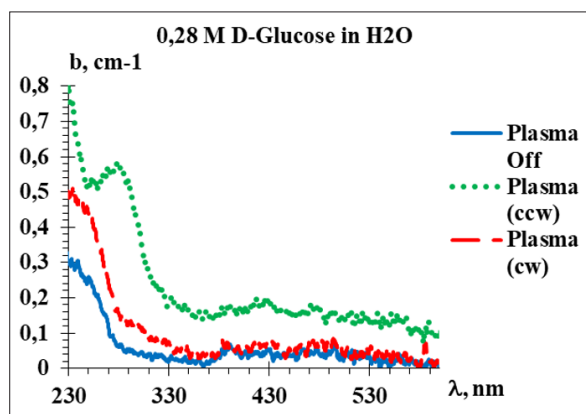


Figure 7: Adsorption spectrum of a solution of 0.28 M D-Glucose in water, both initial (Plasma Off) and plasma-activated (Plasma On) in two modes in the direction of spinning of the CO₂ flow in the system: clockwise - cw and counterclockwise - ccw. The time interval for measurements of adsorption spectra after plasma activation was 10 days.

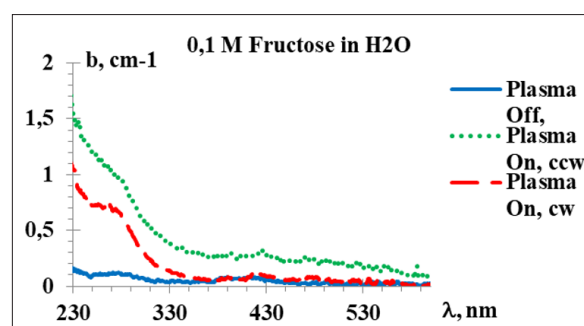


Figure 8: Adsorption spectrum of a solution of 0.1 M Fructose in water, both initial (Plasma Off) and plasma-activated (Plasma On) in two modes in the direction of spinning of the CO₂ flow in the system: clockwise - cw and counterclockwise - ccw. The time interval for measurements of adsorption spectra after plasma activation was 10 days.

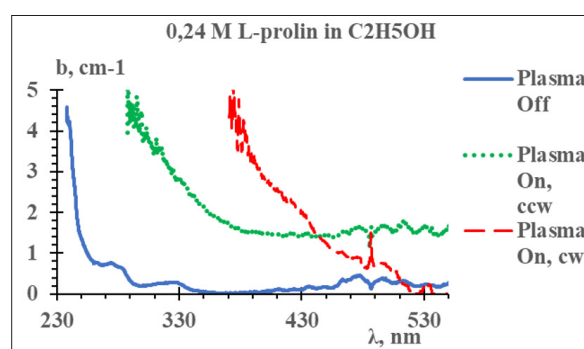


Figure 9: Adsorption spectrum of a solution of 0.24 M L-proline in ethanol, both initial (Plasma Off) and plasma-activated (Plasma On) in two modes of the direction of spinning of the CO₂ flow in the system: clockwise - cw and counterclockwise - ccw. The time interval for measurements of adsorption spectra after plasma activation was 10 days.

As can be seen from the obtained adsorption spectra, plasma activation of solutions leads to a significant decrease in the transparency of solutions in the UV range of light. At the same time, the change in transparency depends on the rotation direction of the reactant particles at the constant energy of plasma spent on generation, both for solutions of chiral sugars and **L-proline**. Adsorption spectra of sugars (Figures 7, 8) are characterized by the appearance of a narrow adsorption band (250-290 nm) with a maximum at $\lambda \approx 270$ nm, specifically in those directions of rotation of gas flows when plasma activation of solutions led to the greatest change in the optical activity of glucose solutions - counterclockwise (Figure 2) and fructose - clockwise (Figure 3). A similar absorption pattern, albeit much less intense, is also characteristic of the initial fructose solution.

Adsorption properties of solutions in the IR ranges of light: As can be seen from the comparison (Figure 10), the transmission spectrum of the initial solution of 0.24 M L-proline in ethanol, and the solvent (pure ethanol), in the IR range practically did not differ from the spectrum of the solvent (pure ethanol), as can be seen from the comparison (Figure 10) of the measured transmission spectra of the initial solution and the spectrum of the used solvent. At the same time, some features of the transmission spectra of solutions C₂H₅OH after plasma activation, which are presented in Figure 11, should be noted, namely their dependence

on the direction of the gas flow rotation in the plasma-chemical system. This includes the appearance of a thin structure in a broad absorption band (3000 - 3500 cm^{-1}) with maxima at 3263, 3337 and 3410 cm^{-1} and increased absorption in the region of 1300 - 2500 cm^{-1} in the counterclockwise rotation direction.

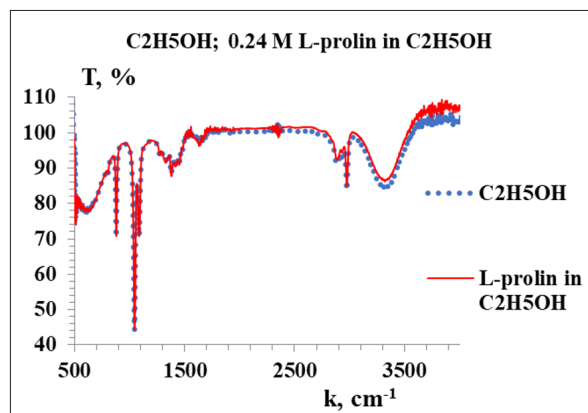


Figure 10: Transmission spectra of the initial solution of 0.24 M L-proline in $\text{C}_2\text{H}_5\text{OH}$ and the spectrum of the used solvent $\text{C}_2\text{H}_5\text{OH}$.

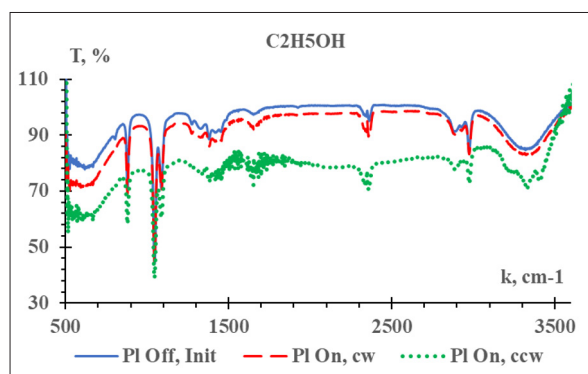


Figure 11: Transmission spectra normalized to the value T (5000 cm^{-1}) of the initial $\text{C}_2\text{H}_5\text{OH}$ and spectra of plasma-activated $\text{C}_2\text{H}_5\text{OH}$ with different directions of the gas flow rotation: cw, ccw.

Raman scattering spectroscopy: The results of IR spectroscopy show that the contribution of the dissolved substance to the transmission spectrum is insignificant compared to the contribution of the solvent. Therefore, the fundamental feature of the results of Raman scattering spectra was the comparative analysis not of the liquid phase solutions themselves, but of the precipitates on the polished surface of polycrystalline BaF_2 that were deposited after liquid phase evaporation from the solution. This approach-obtaining IR transmission spectra while accounting for the presence of L-proline in the solid phase under normal conditions-proved to be more informative. Thus, Figure 12 shows the Raman scattering spectra of both the initial solution of 0.24 M L-proline in $\text{C}_2\text{H}_5\text{OH}$ and its precipitate after evaporation of $\text{C}_2\text{H}_5\text{OH}$. As can be seen, the precipitate spectrum has a much more complex structure.

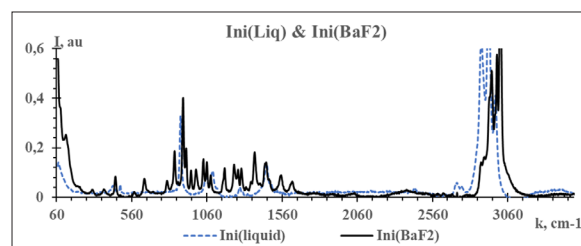


Figure 12: Raman scattering spectra of both the initial solution of 0.24 M L-proline in $\text{C}_2\text{H}_5\text{OH}$ - Ini(liquid) and its precipitate after evaporation of $\text{C}_2\text{H}_5\text{OH}$ - Ini(BaF_2).

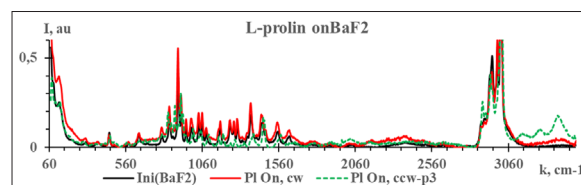


Figure 13: Raman scattering spectra of precipitates from the initial solution of 0.24 M L-proline in $\text{C}_2\text{H}_5\text{OH}$ - Ini (BaF_2), precipitates from solutions of 0.24 M L-proline in $\text{C}_2\text{H}_5\text{OH}$ activated by plasma in different directions of the gas flow rotation: cw(BaF_2), ccw(BaF_2).

Comparative analysis of Raman scattering spectra of precipitates from solutions of 0.24 M L-proline in $\text{C}_2\text{H}_5\text{OH}$ unactivated - Ini(BaF_2) and activated by plasma in different directions of the gas flow rotation: cw(BaF_2), ccw(BaF_2) (Figure 13) also indicates that there is a significant difference in structure of the spectra under modes of plasma activation with different directions of the gas flow rotation: both the disappearance of a number of lines (900, 2989 cm^{-1}) and the appearance of structured broad bands (3100-3500 cm^{-1}) for the ccw mode and the close matching of the spectra of the initial Ini(BaF_2) and cw(BaF_2).

NMR: The parameters of ^{13}C NMR spectra proved to be more sensitive compared to IR spectroscopy and Raman scattering in the studies of 0.24 M solutions of L-proline in $\text{C}_2\text{H}_5\text{OH}$: in the ^{13}C NMR spectra, clear differentiation of lines characteristic of both $\text{C}_2\text{H}_5\text{OH}$ and L-proline is observed (Figure 14).

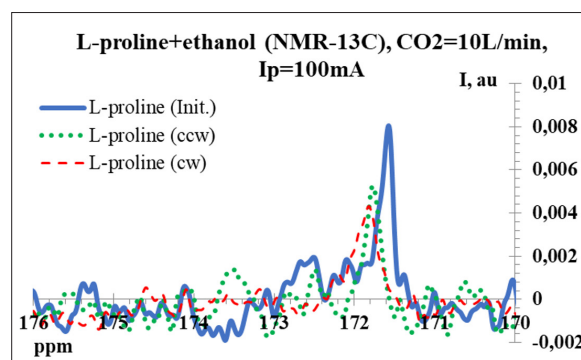


Figure 14: Fragments of ^{13}C NMR spectra: of the initial 0.24 M solution of L-proline in $\text{C}_2\text{H}_5\text{OH}$ - Init, activated by plasma under different directions of gas flow rotation: cw, ccw.

[NIST]. The characteristics of the NMR- ^{13}C $\text{C}_2\text{H}_5\text{OH}$ and L-proline lines observed in the spectra according to NIST and this paper are presented in the Table 1.

Table 1: The characteristics of the NMR-13C C₂H₅OH and L-proline lines according to NIST and this paper

Ethyl alcohol								
NIST			This paper, ppm					
			Plasma Off		Plasma On, ccw		Plasma On, cw	
Assign	ppm	Int	ppm	Int	ppm	Int	ppm	Int
C1	18.39	970	16.17	1	16.07	1	16.05	1
C2	57.79	1000	55.629	0.97	55.638	0.96	55.624	0.97
0.24 M L-proline in Ethyl alcohol								
C1	175.38	218	171.58	0.008	171.740	0.005	171.90	0.0041
C2	62.33	794	60.01	0.013	59.976	0.014	59.949	0.015
C3	47.16	855	44.567	0.012	44.595	0.016	44.604	0.017
C4	29.99	1000	27.954	0.013	27.912	0.017	27.885	0.015
C5	24.79	903	22.687	0.013	22.641	0.0166	22.627	0.0162

As can be seen from the data given in the Table, plasma treatment of the solution leads to a shift of the proline lines by ppm in weak field (for C1, C3 proline and C1, C2 alcohol - an increase in ppm; for C2, C4, C5 proline - in strong field) regardless of the rotation direction, while the shift in the ccw mode is always smaller than in the cw mode. In the vicinity of the C1 and C2 alcohol lines, there are signals of comparable intensity to the proline lines, which are affected by plasma activation in different ways depending on the mode (Figure 15).

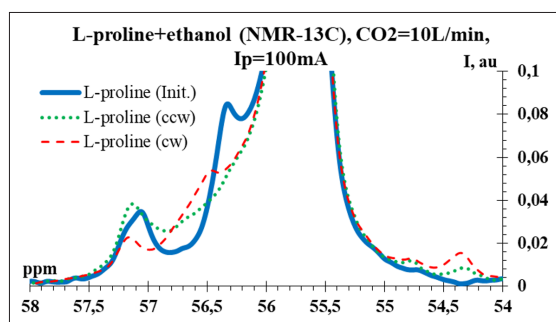


Figure 15: The typical appearance of the proline line in NMR-13C spectra of the initial solution of 0.24 M L-proline in C₂H₅OH - Init, activated by plasma with different directions of the gas flow rotation: clockwise, counterclockwise.

Conclusions

1. The spectral properties of the studied solutions of optically active isomers change significantly after plasma treatment: the nature of the change is influenced both by the direction of the gas flow rotation in the system and by the nature of the optical activity of the dissolved initial isomer.
2. Changes in the transmittance of solutions in the UV range indicate significant destruction of the original hydrocarbon reagent.
3. Spectroscopic studies (in UV and IR ranges, 13C NMR) of L-proline solutions in C₂H₅OH, activated by plasma in a submerged rotating gliding discharge, and Raman scattering of solid-phase precipitates formed after solvent evaporation revealed a significant influence of the gas flow rotation direction on the kinetics of physicochemical processes in the plasma-liquid system.
4. The optical activity of solutions changes randomly within the first few hours after treatment, but the stabilization time

does not exceed 24 hours for solutions of glucose, fructose, proline, and tartaric acid.

5. The main conclusion from the study of solutions after plasma activation in an open non-equilibrium plasma-liquid system, which has significant parameter gradients and does not have a uniform probability in the directions of forced rotation of reagent particles using solutions of chemically pure, optically active reagents, is that plasma activation enables both destructive processes and a significant change in the optical activity of solutions. The change in the optical activity of solutions of polar chiral substances (glucose and fructose) after plasma activation noticeably depends on the direction of forced rotation of reagent particles. The influence of the direction of forced rotation of reagent particles on the change in the optical activity of solutions of non-polar chiral reagents (proline and tartaric acid) was practically absent.

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References

1. Morrison RT, Boyd RN. Optically inactive reagents produce (develop) optically inactive products. Organic Chemistry, 5th ed. Allyn & Bacon Inc. 1987.
2. Jonathan Sarfati. Origin of life: the polymerization problem. CEN Technical Journal. 1998. 12: 263-266.
3. Polak LS, Mikhailov AS. Self-organization in non-equilibrium physicochemical systems. Moscow: Nauka Ed. 1983.
4. Chernyak YaV, Iukhymenko VV, Iukhymenko KV, Oberemok YeA, Tretiakov DD, et al. Plasmachemical synthesis of optically active substances. IEEE Transactions on Plasma Science. 2021. 3: 1050-1054.
5. Chernyak VYa, Fedirchuk II, Iukhymenko VV. Reforming and synthesis of hydrocarbons activated by plasma of gliding discharges in rotating gas flows. "2nd Edition of Chemistry World Conference". 2022. 38: 13-14.
6. Chernyak VYa, Iukhymenko VV, Tretiakov DD, Iukhymenko KV, Oberemok Ye A, et al. Plasma-chemical synthesis of optically active substances. International Conference, Uzhhorod School of Atomic Physics and

Quantum Electronics to the 100th anniversary of the birth of
Professor Ivan Zapisochny. 2023. 38-42.