

Donor-acceptor interactions of iodine with pyridine bases in aqueous and organic media

*E. N. Shubina*¹, *E. A. Flick*^{1*}, and *I. Yu. Zhukova*¹

¹Don State Technical University, 1, Gagarina Square, 344003, Rostov-on-Don, Russia

Abstract. Spectrophotometric studies were carried out on the possibility of the formation of complexes between active forms of iodine and pyridine bases in solvents of different polarities - water (H₂O) and dichloromethane (CH₂Cl₂). Analysis of electronic absorption spectra showed the appearance of different forms of iodine when dissolved in H₂O (220 nm, 290 nm, 360 nm, 460 nm) and in CH₂Cl₂ (240 nm, 300 nm, 504 nm). To prove the possible interaction of various forms of iodine with pyridine bases, absorption spectra of pyridine, 2,6-lutidine, collidine and mixtures (iodine-pyridine base) in H₂O and CH₂Cl₂ were obtained. It has been established that pyridine bases are capable of stabilizing iodine and iodonium ions in the form of donor-acceptor complexes. This is confirmed by intense and wide absorption bands in the spectral region of 250-300 nm (H₂O) and 250-450 nm (CH₂Cl₂), which is associated with charge transfer and the formation of donor-acceptor type complexes, for example, [PyI₂] and [PyI]⁺. The stability constants (K) of the complexes were determined in CH₂Cl₂. In accordance with the obtained spectral and calculated data, the iodine-pyridine complex is the most stable (K = 0.45 l/mol) compared to similar complexes containing pyridine bases with large steric effects. Among the complexes formed between the iodonium ion and pyridine bases, the most stable was the complex of the iodonium ion with collidine (K = 22 l/mol).

1 Introduction

Until the 1990s, X⁺ type halogen ions (X=Br, I), stabilized by a Lewis base pair (L) in the form [L-X-L]⁺, were only an example of donor-acceptor type compounds in which the halogen was present in oxidation state plus 1 [1]. Among complex halogen compounds X⁺ as stabilizing Lewis bases, the description of pyridine derivatives (Py) with a substituent in the 4th position predominates in the scientific literature [2]. The complexes with the largest steric bulk are mentioned, including 2,6-dimethylpyridine (2,6-lutidine) and 2,4,6-trimethylpyridine (collidine) around the I⁺ ion [3-6]. Over time, such structures have found application in various organic transformations as a soft source of electrophilic halogen [1, 7-10]. For example, the commercially available Barluenga reagent is [I(Py)₂]BF₄, a common reagent for iodination [11], to which the chemistry of iodine (I) owes its fame.

* Corresponding author: eaff@yandex.ru

In the reactions of the electrocatalytic oxidative transformation of alcohols in a two-phase medium (water (H₂O)/dichloromethane (CH₂Cl₂)) using the I⁻/I₂ mediator system, a nitroxide radical as a catalyst and a pyridine base as a cocatalyst [12], iodine acts as an oxidizing agent. The presence of a free active form of iodine is undesirable, especially in the case of alcohols that are sensitive to the action of such an oxidizing agent. Under the conditions of the electro oxidative transformation of alcohols, the complex of the active form of iodine with a pyridine base is more preferable, since it is a mild oxidizing agent and promotes the selective conversion of various alcohols into carbonyl compounds. There is no data in the literature on the formation and stability of such complexes under conditions of electro oxidative transformation of alcohols in a two-phase electrolyte, therefore, studies of donor-acceptor interactions between the generated active forms of iodine, including iodine (I), and structurally dissimilar pyridine bases are relevant.

2 Experimental part

During the research, reagents from the companies «Acros», «REAHIM», and «NevaReaktiv» were used without additional purification.

To prepare aqueous solutions, double distillate was used, upon production of which a 3% solution of potassium permanganate was added to distilled water to destroy organic impurities. The destruction of traces of surfactants was carried out by boiling double distillate with activated carbon for five minutes. The purity of the dichloromethane solvent was ensured by double distillation of the «special purity» sample.

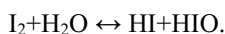
Spectrophotometric studies were carried out in the UV and visible regions of the spectrum. Absorption spectra were recorded using a Spectrophotometer-2000 spectrophotometer in the wavelength range 200-700 nm. Samples of solutions were placed in quartz optical cuvettes with an optical length of 10 mm.

All measurements in the UV and visible regions of the spectrum were carried out at least three times, the results obtained were statistically processed, taking the confidence level equal to 0.95.

To calculate the equilibrium constants (K) of the complexation reaction, a graphical method was used [13].

3 Discussion of results

In order to identify various forms of iodine and the possibility of their interaction with pyridine bases (Py, 2,6-lutidine, collidine) in the UV and visible range, the behaviour of iodine in H₂O and CH₂Cl₂ was first studied, i.e. The conditions for the appearance of different forms of iodine in these solvents were modelled. One of the most important characteristics of any solvent is its dielectric constant (ϵ), which reflects its ability to participate in the dissociation of a substance into positive and negative ions in solution. A more polar, "active" solvent is H₂O ($\epsilon=80$) [14]. It, to a greater extent than CH₂Cl₂ ($\epsilon = 9.1$), promotes the dissociation of I₂ with the formation of its active forms - iodonium and iodide ions: $I_2 \leftrightarrow I^+ + I^-$ [15]. The formation of atomic iodine (I•) is unlikely to be detected spectrophotometrically, because as it is a short-lived particle, and the authors of [16] found only kinetic evidence of its formation. It should be taken into account that in H₂O iodine is partially hydrolysed in the presence of free H⁺ and OH⁻ ions [17]:



However, I_2 is poorly soluble in H_2O ; it dissolves more actively in alcohol and other organic solvents [18].

Spectrophotometric studies confirmed the appearance of different forms of iodine when dissolved in H_2O (Figure 1, curve 1) and CH_2Cl_2 (Figure 1, curve 2), which manifests itself in the presence of different absorption bands of I_2 and its active forms, arising due to changes in the polarity of the solvent. In the electronic absorption spectra, with increasing polarity of the solvent, a hypsochromic shift (“blue shift”) occurs. It should be taken into account that in the considered spectral region from 250 to 550 nm there are mainly bands of $n \rightarrow \pi^*$ transitions, which are characterized by low intensity (corresponding to D up to 1.0 ($\epsilon = 10-1000$)) and are characteristic of intramolecular charge transfer from donor to acceptor [19].

The main absorption peak of I_2 is observed at 460 nm (H_2O) and 504 nm (CH_2Cl_2) [20]; and there is also an absorption peak of iodide ion (I^-) at 220 nm (H_2O) and 240 nm (CH_2Cl_2) and absorption bands at 360 nm (H_2O) and 300 nm (CH_2Cl_2), which does not contradict the data of the work [21].

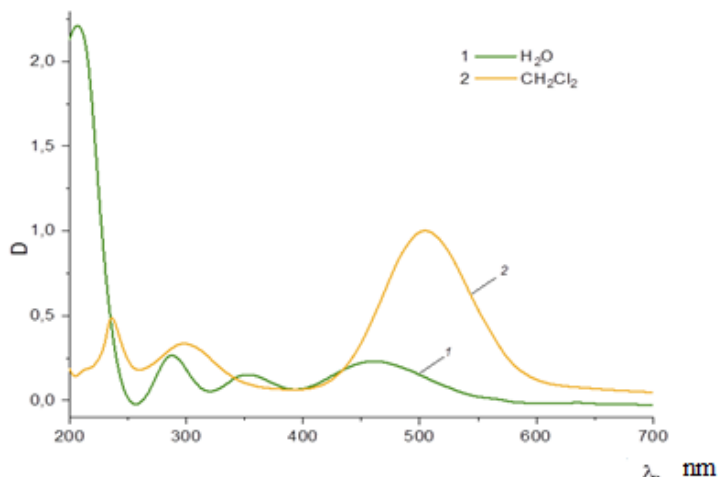


Fig. 1. Electronic absorption spectra of 10^{-3} M iodine: 1 – in H_2O ; 2 – in CH_2Cl_2 .

Probably, a more polar solvent (H_2O) polarizes the I_2 molecule, promotes the dissociation and formation of iodonium (I^+) (290 nm) and iodide (I^-) (220 nm) ions, and possibly other forms of iodine (360 nm), such as I_3^- [16]. In the spectrum of I_2 in CH_2Cl_2 , a hyperchromic effect and, at the same time, a bathochromic shift to 504 nm (related to I_2) are observed, i.e. absorption bands shift towards longer wavelengths. Under these conditions, a bathochromic shift is also characteristic of the peaks related to the iodine anion – I^- (240 nm) and iodonium ion – I^+ (300 nm).

To confirm the possible interaction of various forms of iodine with pyridine bases, absorption spectra of I_2 , Py, 2,6-lutidine (2,6-Lut), collidine (Collid) and mixtures (iodine-pyridine base) in H_2O were obtained (Figures 2, 3) and CH_2Cl_2 (Figures 4, 5).

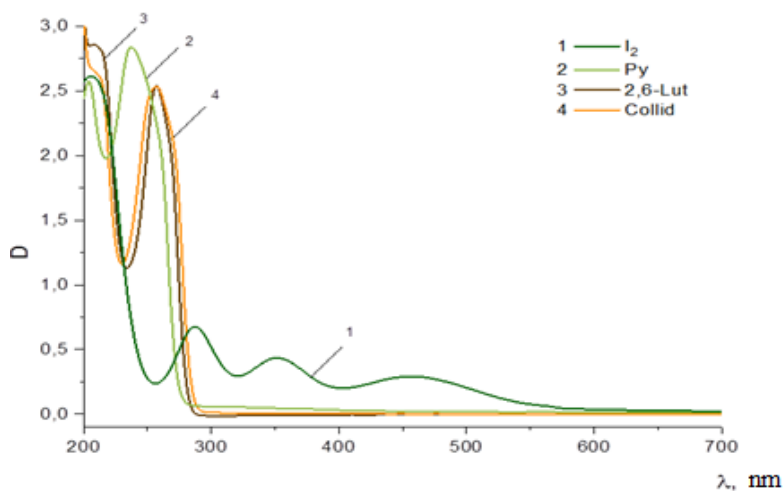


Fig. 2. Electronic absorption spectra in H₂O: 1 – $1 \cdot 10^{-3}$ M iodine; 2 – $1 \cdot 10^{-3}$ M pyridine; 3 – $1 \cdot 10^{-3}$ M 2,6-lutidine; 4 – $1 \cdot 10^{-3}$ M collidine.

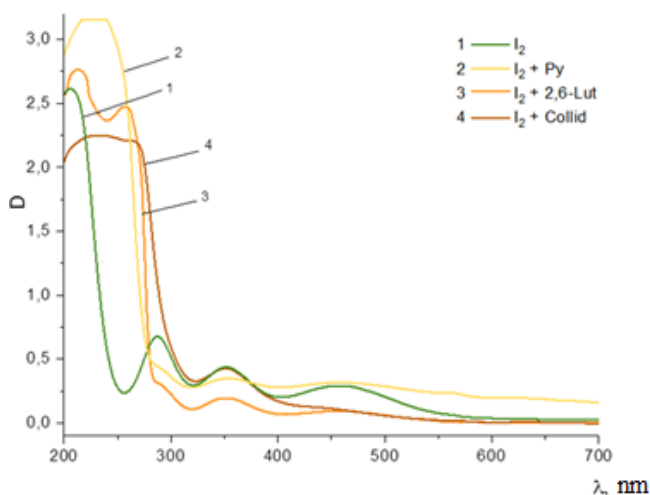


Fig. 3. Electronic absorption spectra in H₂O mixtures: 1 – $1 \cdot 10^{-3}$ M iodine + $1 \cdot 10^{-3}$ M pyridine; 2 – $1 \cdot 10^{-3}$ M iodine + $1 \cdot 10^{-3}$ M 2,6-lutidine; 3 – $1 \cdot 10^{-3}$ M iodine + $1 \cdot 10^{-3}$ M collidine.

The absorption spectra of I₂, pyridine bases (Figure 2) and iodine-pyridine base mixtures (Figure 3) in H₂O are different. When pyridine bases are added to an iodine solution, a significant decrease in the intensity of the absorption bands at 290 nm (I⁺) and 460 nm (I₂) is observed. In the spectrum of the I₂ – Collid mixture, these absorption bands almost completely disappear. Probably, of the studied pyridine bases, Collid exhibits the greatest activity towards I₂ and the I⁺ ion, binding them into complexes. This is reflected in the appearance of the hyperchromic effect - a broad absorption band in the region of 220-280 nm (Figure 3), which is associated with charge transfer and the formation of donor-acceptor type complexes [20], for example, [PyI]⁺ and/or [PyI₂]. The [PyI₂] complex can undergo heteropolar dissociation into [PyI]⁺ and I⁻. The resulting I⁻ ion reacts with I₂ and

gives the I_3^- ion, the absorption band of which is in the range from 330 to 370 nm (Figure 3).

Complexes $[PyI]^+$ and/or $[PyI_2]$ can also appear from the following equilibrium:



The electronic absorption spectra in CH_2Cl_2 for I_2 , pyridine bases (Figures 1, 4) and iodine-pyridine base mixtures (Figure 5) differ from their spectra in H_2O .

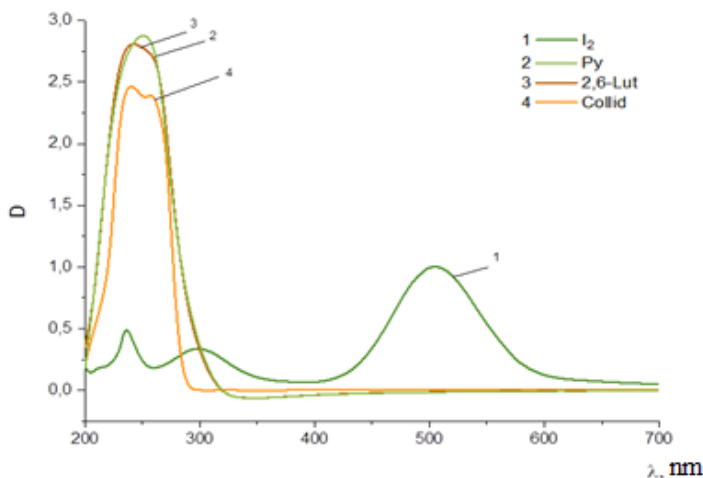


Fig. 4. Electronic absorption spectra in CH_2Cl_2 : 1 – $1 \cdot 10^{-3}$ M iodine; 2 – $1 \cdot 10^{-3}$ M pyridine; 3 – $1 \cdot 10^{-3}$ M 2,6-lutidine; 4 – $1 \cdot 10^{-3}$ M collidine.

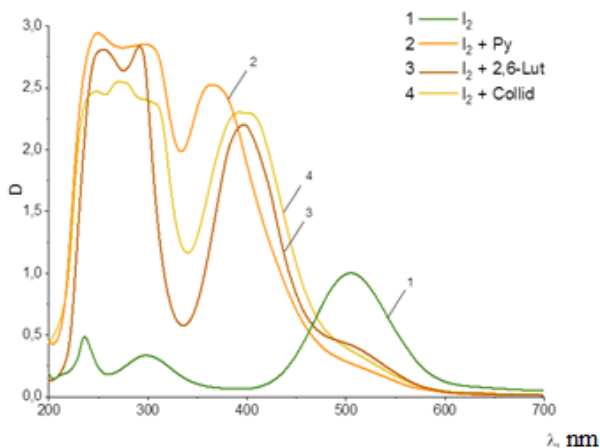


Fig. 5. Electronic absorption spectra in CH_2Cl_2 mixtures: 1 – $1 \cdot 10^{-3}$ M iodine; 2 – $1 \cdot 10^{-3}$ M iodine + $1 \cdot 10^{-3}$ M pyridine; 3 – $1 \cdot 10^{-3}$ M iodine + $1 \cdot 10^{-3}$ M 2,6-lutidine; 4 – $1 \cdot 10^{-3}$ M iodine + $1 \cdot 10^{-3}$ M collidine.

In the spectra of mixtures (Figure 5), there is practically no absorption band at 504 nm, which belongs to I_2 , but high-intensity bands are observed in the region of 350–450 nm (corresponding to a complex of the pyridine base- I_2 type) and 250–300 nm (corresponding to a complex of the type pyridine base- I^+). A hypsochromic shift occurs due to the

formation of complexes between the pyridine base and I_2 , as well as the pyridine base and I^+ . This does not contradict studies [22], which describe the formation of a positively charged complex of the $[Bis(Py)I]^+$ type.

Thus, the increase in absorption intensity in the spectral region of 250-300 nm (H_2O) (Fig. 3) and especially in the region of 250-450 nm (CH_2Cl_2) (Fig. 5) is associated with charge transfer, i.e. a shift in electron density from the donor (pyridine base) to the acceptor (I^+ , I_2) [19] and the formation of complexes of the donor-acceptor type, for example, $I_2+2Py \leftrightarrow [Py_2I]^+I^-$ [18].

In order to determine the stability of the resulting $[PyI_2]$ and $[PyI]^+$ complexes, the equilibrium constants (K) of the complexation reaction (stability constants) in CH_2Cl_2 were calculated, since water can stabilize individual ions, which in turn will lead to inhibition of complexation processes [23]. To calculate the K of complex compounds, we used the data from the spectra of mixtures of I_2 – pyridine base (Py, 2,6-Lut, Collid) and the graphical method [13]. Electronic absorption spectra in CH_2Cl_2 of mixtures of I_2 + pyridine base are presented in Figures 6-8. The data necessary to determine the K value of the complexes is given in Tables 1, 2.

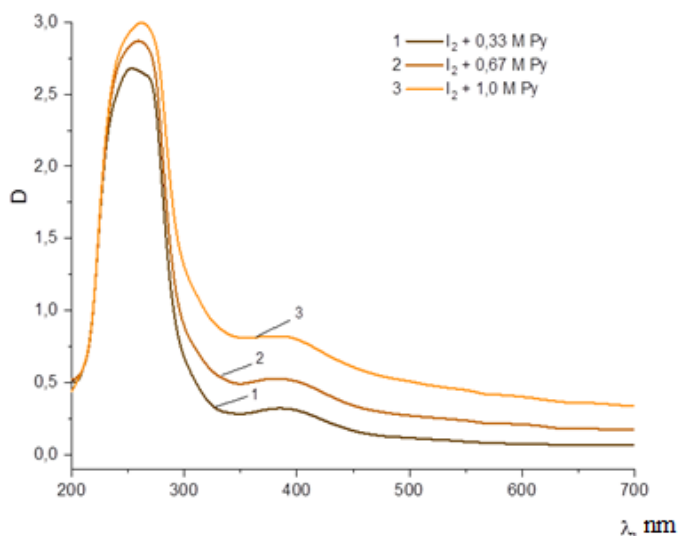


Fig. 6. Electronic absorption spectra in CH_2Cl_2 mixture: 1 – $1 \cdot 10^{-4}$ M iodine + 0.33 M pyridine; 2 – $1 \cdot 10^{-4}$ M iodine + 0.67 M pyridine; 3 – $1 \cdot 10^{-4}$ M iodine + 1.0 M pyridine.

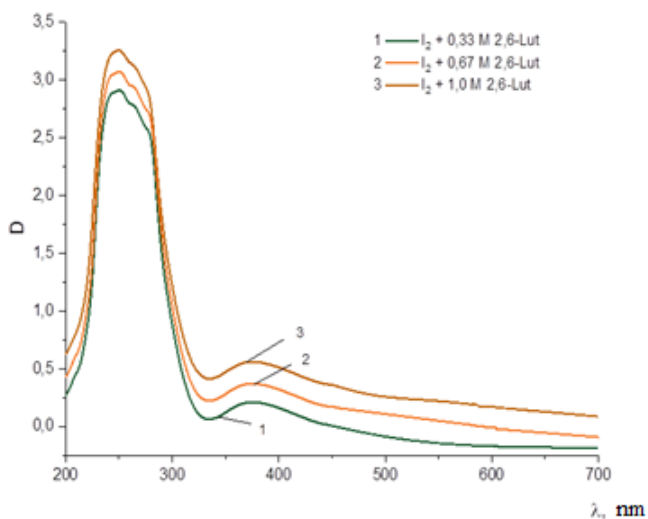


Fig. 7. Electronic absorption spectra in CH₂Cl₂ mixture: 1 – 1·10⁻⁴ M iodine + 0.33 M 2,6-lutidine; 2 – 1·10⁻⁴ M iodine + 0.67 M 2,6-lutidine; 3 – 1·10⁻⁴ M iodine + 1.0 M 2,6-lutidine.

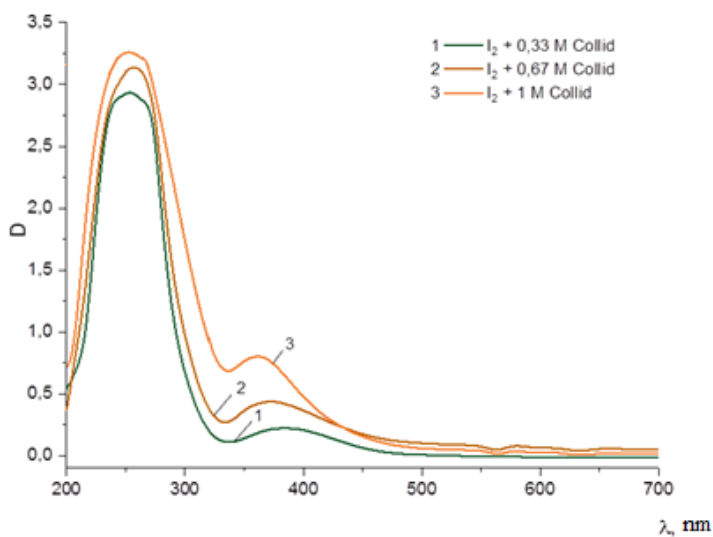


Fig. 8. Electronic absorption spectra in CH₂Cl₂ mixture: 1 – 1·10⁻⁴ M iodine + 0.33 M collidine; 2 – 1·10⁻⁴ M iodine + 0.67 M collidine; 3 – 1·10⁻⁴ M iodine + 1.0 M collidine.

Table 1. Data for determining the stability constants (KP) of the iodonium ion-pyridine base complexes at the initial iodine concentration $[I_2]_0 = 1 \cdot 10^{-4}$ mol/l.

Wavelength, nm	Pyridine base	$[C_5H_5N]_0$, mol/l	$\frac{1}{[C_5H_5N]_0}$, (l)/mol	D	$\frac{[I_2]_0 l}{D} \times 10^4$, (mol·cm)/l	ϵ , l/(mol·cm)	lg ϵ	K, l/mol
290	Pyridine	0.33	3.03	2.676	0.373	33333	4.52	12
		0.67	1.49	2.869	0.349			
		1.0	1.0	3.01	0.332			
	2,6-Lutidine	0.33	3.03	2.911	0.394	33333	4.52	20
		0.67	1.49	3.07	0.367			
		1.0	1.0	3.25	0.365			
	Collidine	0.33	3.03	2.933	0.341	33333	4.52	22
		0.67	1.49	3.156	0.317			
		1.0	1.0	3.257	0.307			

Table 2. Data for determining the stability constants (KP) of iodine-pyridine base complexes at an initial iodine concentration $[I_2]_0 = 1 \cdot 10^{-4}$ mol/l.

Wavelength, nm	Pyridine base	$[C_5H_5N]_0$, mol/l	$\frac{1}{[C_5H_5N]_0}$, (l)/mol	D	$\frac{[I_2]_0 l}{D} \times 10^4$, (mol·cm)/l	ϵ , l/(mol·cm)	ϵ , l/(mol·cm)	K, l/mol
390	Pyridine	0.33	3.03	0.324	3.09	25000	4.398	0.45
		0.67	1.49	0.530	1.89			
		1.0	1.0	0.827	1.21			
	2,6-Lutidine	0.33	3.03	0.203	4.93	33333	4.523	0.19
		0.67	1.49	0.373	2.68			
		1.0	1.0	0.561	1.78			
	Collidine	0.33	3.03	0.226	4.42	50000	4.699	0.14
		0.67	1.49	0.436	2.16			
		1.0	1.0	0.801	1.64			

In accordance with the results obtained, dependencies were constructed $\frac{[I_2]_0 l}{D} = f\left(\frac{l}{[pyridine]_0}\right)$ (Figures 9, 10).

From the slope of the obtained straight lines ($\tan \alpha$) and the points of their intersection with the ordinate axis $\left(\frac{[I_2]_0 l}{D}\right)$, the absorption coefficients (ϵ) and stability constants of complexes (K) for complexes of iodonium ion-pyridine base were determined (Table 1) and iodine-pyridine base (Table 2).

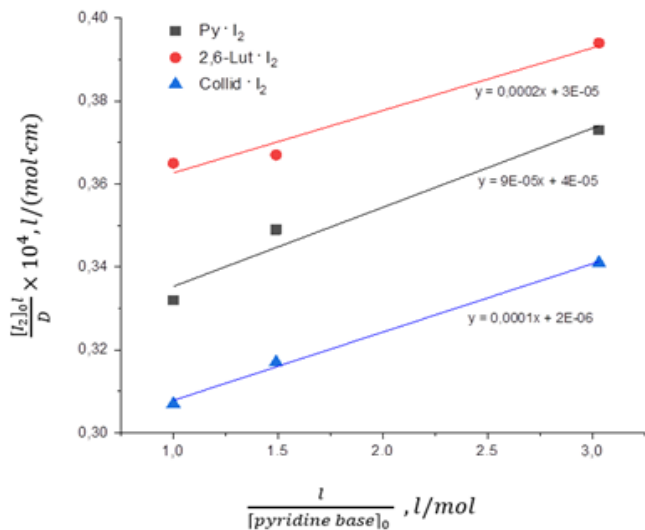


Fig. 9. Graph of dependence $\frac{[I_2]_0 l}{D} = f\left(\frac{l}{[\text{pyridine base}]_0}\right)$ for determining absorption coefficients (ϵ) and equilibrium constants (K) of iodonium ion-pyridine base complexes (band absorption at 290 nm).

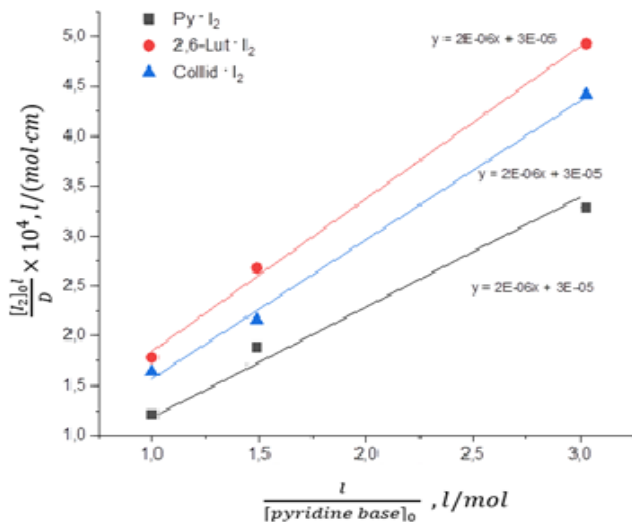


Fig. 10. Dependency graph $\frac{[I_2]_0 l}{D} = f\left(\frac{l}{[\text{pyridine base}]_0}\right)$ for determining the absorption coefficients (ϵ) and equilibrium constants (KP) of iodine-pyridine base complexes (absorption band at 390 nm).

The iodine-collidine complex is less stable ($K = 0.14$ l/mol) (Table 2), therefore it dissociates better and molecular iodine is present in the solution. The iodine-2,6-lutidine complex is slightly different in stability ($K = 0.19$ l/mol) (Table 2) from the iodine-collidine complex. The iodine-pyridine complex, according to the obtained spectral and calculated data, is the most stable ($K = 0.45$ l/mol) of those considered. The presence of substituents in positions close to the donor atom creates steric hindrances during complex formation, caused by a change in the planar configuration of the ligand, which entails disturbances in the conjugation system and the stability of the complex as a whole. Methyl groups at positions 2 and 6 effectively shield the nitrogen atom at position 1, thereby reducing the strength of binding to the iodine molecule.

When considering the data on the formation of complexes between the iodonium ion and pyridine bases, it was found that the most stable are the complexes of the iodonium ion with collidine ($K = 22$ l/mol) and 2,6-lutidine ($K = 20$ l/mol). In this form, the active iodonium ion is a milder oxidizing agent.

4 Conclusion

Analysis of electronic absorption spectra confirmed the appearance of different forms of iodine in water and dichloromethane. Spectrophotometric studies of the behaviour of active forms of iodine and pyridine bases, as well as their mixtures in the UV and visible regions of the spectrum showed that pyridine bases are capable of stabilizing iodine and iodonium ion in the form of complexes that differ in stability. The iodine-pyridine complex is more stable compared to complexes of iodine and pyridine bases with large steric effects, such as 2,6-lutidine and collidine. It has been established that pyridine bases also form complexes with the active form of iodine - iodonium ion. According to calculations, the most stable is the iodonium ion-collidine complex, which makes this pyridine base the most promising co-catalyst in reactions of electro oxidative transformation of alcohols with the participation of the I/I_2 mediator system, nitroxide radical as a catalyst and pyridine base as a co-catalyst, especially in the case of substrates sensitive to the action of iodine.

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