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Reaction of 2-naphthol with substituted benzenediazonium salts in [bmim][BF_4]

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Abstract

Diazo-coupling reaction of 4-substituted benzenediazonium tetrafluoroborates with 2-naphthol in [bmim][BF_4] has been studied in the presence of triethylamine (B) and triethylammonium tetrafluoroborate (BH^+) (1:1) under the conditions of pseudo-first-order reaction at 25 °C. It was found that the observed rate constant (k_{obs}) of the diazo-coupling reaction increases linearly with increasing concentration of triethylamine. On the basis of kinetic isotope effect measured with 1-deuterio-2-naphthol ($k_H/k_D = 1$), it was shown that the linear increase in k_{obs} vs. [B] is not due to general base catalysis, and the rate-limiting step is, like in molecular solvents, the formation of Wheland tetrahedral intermediate. This fact was also confirmed by the value of the reaction constant $\rho^+ = 1.2 \pm 0.1$. The linear increase in k_{obs} vs. [B] was explained by the effect of increasing concentration of [B] upon the activity coefficient γ_B and, hence, also upon the position of the acid–base equilibrium between the nonreactive 2-naphthol and reactive 2-naphthoxide or its proton-transfer complex (ion-pair). This acid–base equilibrium was studied using 4-nitrophenol as a model. It was proved that even at a constant ratio of [B]/[BH^+] the concentration of 4-nitrophenoxide (or its proton-transfer complex with triethylamine) increases with increasing concentration [B]. Furthermore, it was found that triethylamine in [bmim][BF_4] exhibits a comparable basicity as 4-nitrophenoxide ($\Delta pK_a \approx 0$), while their basicities in water differ by more than 3.5 orders of magnitude.

Keywords: Ionic liquids; Diazo-coupling; Activity coefficients

1. Introduction

Room temperature ionic liquids (RTILs) are attracting increasing attention as alternative solvents because of their unique properties. Perhaps, the most important example of their application is their use as substitutes for common volatile organic solvents (VOCs) in organic and inorganic syntheses [1] and especially catalytic reactions [2]. There was published a lot of electrophilic [1] and nucleophilic [3] reactions in the literature in which the presence of ionic liquid increased yield or shortened reaction time. However, the reaction that was almost not studied in ionic liquids is diazo-coupling. The only work dealing with diazo-coupling [4] in [hmim][PF_6] and [hmim][ClO_4] concerns reaction of diazonium salt of sulfanilic acid with *N*,*N*-dimethylaniline giving methyl orange in much more better yield as compared with reaction in acetic acid. This reaction proceeded in "neutral" medium, i.e. without the addition of base.

The aim of this work is to study diazo-coupling reaction of substituted benzenediazonium salts **1a–d** with 2-naphthol in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) giving substituted 1-phenylazo-2-naphthols (Scheme 1). This work also extends previously published paper [5] dealing with the synthesis of such compounds in ionic liquids.

Except for potential applicability in dye industry, the reaction was chosen because it is well characterised in water including influence of substituents as well [6]. Moreover, the chemo-, regio- and stereoselectivities as well as kinetic behaviour of many reactions are deeply influenced by the solvent. In

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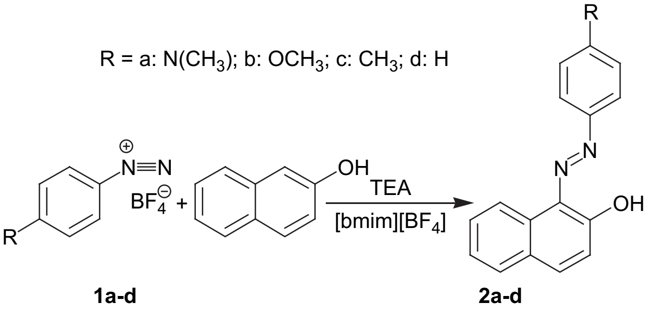


Scheme 1.

contrast, the limited number of systematic kinetic investigations in ionic liquids is available although the absence of such investigations drastically reduces the possibility of correlating the reaction courses to some ionic liquid properties such as polarity, nucleo- and electrophilicity, coordination ability, etc.

2. Results and discussion

The kinetics of diazo-coupling reaction of benzenediazonium tetrafluoroborates **1a–d** with 2-naphthol was studied at the conditions of pseudo-first-order reaction in buffers containing triethylamine (B) and triethylammonium tetrafluoroborate (BH^+) in ratio 1:1 at 25 °C. It means that analytical concentrations of 2-naphthol (c_N) and both buffer components ($[BH^+]$ and [B]) were at least 1 order of magnitude higher than concentration of diazonium salt ($c_S = 8 \times 10^{-5}\ \mathrm{mol\,l^{-1}}$) and they were virtually constant during the reaction course.

It was possible to study reactions of benzenediazonium tetrafluoroborates carrying electron-donating groups only. Diazo-coupling reaction of derivatives carrying electron-withdrawing groups was very fast so that it was impossible to determine observed rate constants. Because of the high viscosity of [bmim][BF_4] (233 cP), the overall time of reaction for such derivatives was shorter than the time needed for thorough mixing of components.

In order to avoid the potential effects of other anions present in the reaction mixture, we chose the highly stable tetrafluoroborate salts of benzenediazonium and triethylammonium tetrafluoroborate for this study.

At first, we dealt with the problem of the necessity of addition of the base in this reaction. It was found that, like in the diazo-coupling reaction carried out in water or other solvents, the 2-naphthol itself does not undergo the reaction, and only after addition of a base (triethylamine, *N*-methylmorpholine, etc.) it is possible to observe the formation of the product, i.e. 1-(4-substituted phenyldiazenyl)-2-naphthols (**2a–d**).

For the detailed study, we chose triethylamine because (1) it is soluble in [bmim][BF_4]; (2) its basicity in water ($pK_a = 10.75$) [7] is greater than the acidity of 2-naphthol ($pK_a = 9.57$) [8]; (3) it is a tertiary amine, which in fact prevents coupling of diazonium salt at the nitrogen atom.

The diazo-coupling reaction can be described by general Scheme 2 and, using the Bodenstein steady-state approximation, also by general kinetic Eq. (1).

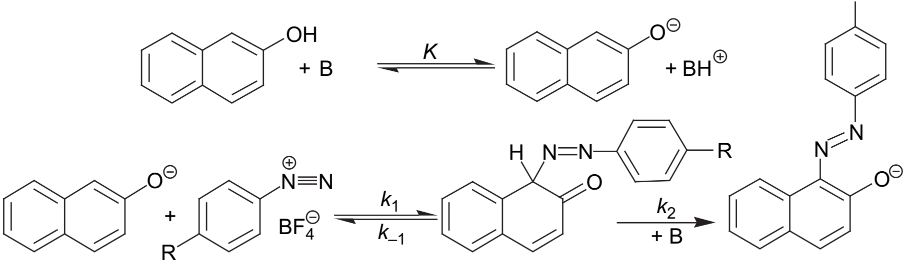
$$v = \frac{k_1 k_2[\mathrm{B}]}{k_{-1} + k_2[\mathrm{B}]}\left[\mathrm{ArN}_2^+\right]\left[\mathrm{ArO}^-\right] \tag{1}$$

In water [9], polar protic [10], polar aprotic [10] as well as non-polar [11] solvents the rate-limiting step of reaction is the reaction of 2-naphthoxide with diazonium salt (k_1), hence Eq. (1) changes to Eq. (2), where the catalyst base does not make itself felt kinetically:

$$v = k_1\left[\mathrm{ArN}_2^+\right]\left[\mathrm{ArO}^-\right] \tag{2}$$

However, the monitoring of diazo-coupling reaction kinetics in [bmim][BF_4] showed that the observed rate constant increases linearly with increasing concentration of triethylamine [B]. The data measured are summarized in Table 1.

Such finding is usually ascribed to the operation of general base catalysis, in which the proton is transferred from the substrate to the catalyst base in the rate-limiting step. In the diazo-coupling reactions of 2-naphthols in both water and non-aqueous media, the dependence of k_{obs} on the base concentration was observed only exceptionally [6,12,13] and only with the eight-substituted derivatives. The phenomenon of general base catalysis is closely associated with the presence of a hindering group at the *peri* position [13] of the 2-naphthol derivative. Steric effect of the *peri* group operates mainly in the second step of the reaction (i.e. base catalyzed decomposition of the intermediate to product) so that k_2 is lowered whereas k_{-1} is not influenced. In such case, Eq. (1) changes to



Scheme 2.

Table 1
Experimental conditions and results of kinetic studies

$V_{[\mathrm{bmim}][\mathrm{BF4}]}$ (µl)[a]	V_B (µl)[a]	V_BH (µl)[a]	[B] (mol l^{-1})	**1a**, $10^2 \times k_\mathrm{obs}$ (s^{-1})	**1b**, $10^2 \times k_\mathrm{obs}$ (s^{-1})	**1c**, $10^2 \times k_\mathrm{obs}$ (s^{-1})	**1d**, $10^2 \times k_\mathrm{obs}$ (s^{-1})
810	75	75	0.0075	–	0.76	1.09	0.626
760	100	100	0.01	0.038	1.46	2.83	3.68
710	125	125	0.0125	–	2.17	5.34	7.26
660	150	150	0.015	–	2.77	6.60	10.9
610	175	175	0.0175	–	3.56	8.71	–
560	200	200	0.02	0.148	4.40	11.9	–
510	225	225	0.0225	–	5.08	–	–
360	300	300	0.03	0.338	–	–	–
160	400	400	0.04	0.430	–	–	–
0	500	500	0.05	0.609	–	–	–
Values of slopes k_obs vs. [B] k (l mol s^{-1})				0.142	2.89	8.34	14.70

[a] Volumes of stock solutions charged into cell (see Section 4).

Eq. (3) at low concentrations of the catalyst base (where it is $k_2[\mathrm{B}] \ll k_{-1}$):

$$v = \frac{k_1 k_2[\mathrm{B}]}{k_{-1}}\left[\mathrm{ArN}_2^+\right]\left[\mathrm{ArO}^-\right] = K_1 k_2\left[\mathrm{ArN}_2^+\right]\left[\mathrm{ArO}^-\right][\mathrm{B}]. \qquad (3)$$

The overall rate of diazo-coupling reaction followed at the pseudo-first-order conditions (c_N, [BH$^+$] and [B] $\gg$ [ArN$_2^+$]) can be expressed by Eq. (4).

$$v = k_\mathrm{obs}\left[\mathrm{ArN}_2^+\right]. \qquad (4)$$

Hence, the observed rate constant, k_obs, is given by Eq. (5):

$$k_\mathrm{obs} = K_1 k_2[\mathrm{ArO}^-][\mathrm{B}] = k_\mathrm{B}[\mathrm{B}]; \qquad (5)$$

Hence, the finding of linear dependence between k_obs and concentration of triethylamine [B] suggests that, in contrast to other solvents, the decomposition of the Wheland intermediate could be the rate-limiting step in the reactions of 2-naphthols without 8-substituents. In order to be able to confirm or reject this hypothesis, we prepared 1-deuterio-2-naphthol, which should exhibit the kinetic isotope effect ($k_\mathrm{H}/k_\mathrm{D} > 1$). The measurements of the observed rate constant of diazo-coupling reaction of **1a–d** with 1-deuterio-2-naphthol at otherwise comparable conditions did not reveal any kinetic isotope effect (i.e. $k_\mathrm{H}/k_\mathrm{D} = 1$). This finding unambiguously proves that the rate-limiting step does not consist in the base catalyzed decomposition of the Wheland intermediate, and the linear dependence of k_obs on concentration of triethylamine must be explained in some other way, not as a manifestation of general base catalysis. The fact that the formation of the Wheland intermediate is rate limiting also follows from the value of the reaction constant $\rho^+ = 1.2 \pm 0.1$ obtained by plotting the Hammett correlation of $\log k(\mathbf{1a{-}d})$ against σ_p^+ values of the individual substituents, where the constants $k(\mathbf{1a{-}d})$ correspond to slopes of the linear dependences of k_obs vs. [B].

However, the formation of the Wheland intermediate is not assisted by base, hence the only step that can be affected by base is the rapid pre-equilibrium between non-reactive 2-naphthol and reactive 2-naphthoxide.

Literature[14] states that proton transfers between phenols and tertiary amines proceed through the phase of hydrogen-bonded complex and proton-transfer complex (ion-pair), which can finally decompose, depending on the solvation abilities of solvents, to form free ions (Scheme 3).

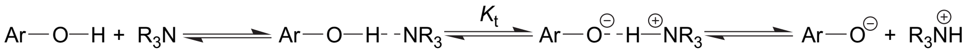
The proton-transfer constant K_t generally depends [14a] on the difference between the pK_a's of the proton acceptor and of the proton donor in water (Eq. (6)).

$$\log K_\mathrm{t} = \xi\,\Delta\mathrm{p}K_\mathrm{a} - \delta \qquad (6)$$

This equation holds for a given family of complexes in a given solvent. The ξ parameter (common values are between 0.2 and 0.9) describes the "hardness" of the hydrogen bond while δ parameter depends on the dielectric constant of the medium.

Because of the much greater separation of charge in the proton-transfer complexes, their formation should be favored by an increase in the polarity of the solvent. Beyond a certain polarity the complex dissociates into its constituent ions [14b].

The polarity of ionic liquids has been empirically determined by means of a variety of solvatochromic probe dyes [15]. The values of empirical polarity parameters found for a number of 1-alkyl-3-methylimidazolium ionic liquids show that the polarity of these salts is comparable to that of short-chain alcohols. From this point of view, the polarity of ionic liquids fits quite well into existing empirical solvent polarity scale for molecular solvents. It appears that ionic liquids behave not as superpolar but as quite normal polar solvents. Nevertheless, similar ionic liquids are capable of behaving quite



$$\mathrm{Ar{-}O{-}H} + \mathrm{R_3N} \rightleftharpoons \mathrm{Ar{-}O{-}H\cdots NR_3} \overset{K_\mathrm{t}}{\rightleftharpoons} \mathrm{Ar{-}O^{\ominus}\cdots H{-}\overset{\oplus}{N}R_3} \rightleftharpoons \mathrm{Ar{-}O^{\ominus}} + \mathrm{R_3\overset{\oplus}{N}H}$$

Scheme 3.

differently when used in organic synthesis [16] or in other applications. Therefore, characterization of ionic liquids on the basis of multiple solvation interactions [17] was carried out.

In order to explain the anomalous kinetic course of the diazo-coupling reaction studied, we tried to monitor the acid–base equilibria between 2-naphthol and triethylamine using UV–vis spectroscopy. Unfortunately, we found that the spectrum of 2-naphthol is practically the same both with and without the addition of triethylamine, which means that the reactive proton-transfer complex (ion-pair) and/or the free 2-naphthoxide are only present at very low concentrations. Therefore, for further studies we chose 4-nitrophenol, whose acidity in water is approximately 2.5 orders higher ($pK_a = 7.16$) [18], and the absorption maxima of both non-dissociated and dissociated forms lie in the region in which [bmim][BF_4] does not absorb.

It was found that in buffers with varying ratios of triethylamine to triethylammonium tetrafluoroborate there occurs a decrease in the band corresponding to the non-dissociated 4-nitrophenol and/or its hydrogen-bonded complex ($\lambda_{max} = 320$ nm) and an increase in the band corresponding to the proton-transfer complex (ion-pair) or 4-nitrophenoxide anion ($\lambda_{max} = 425$ nm). The said pairs cannot be differentiated spectrally [19]. For instance, in solutions of aromatics it was proved on the basis of adiabatic dilution calorimetry [14a] that phenols form with tributylamine a hydrogen-bonded complex that possesses a practically identical spectrum [14b] as the non-dissociated phenol.

From what has been said it follows that pK_a values of 4-nitrophenol and triethylammonium ion in [bmim][BF_4] are very close, which indicate specific solvation effects as compared with water, in which the pK_a difference is more than 3.5 pK_a units. Hence, 2-naphthol, which is ca. 2.4 orders of magnitude less acidic than 4-nitrophenol in water, will be predominantly present as the non-reactive hydrogen-bonded complex in [bmim][BF_4].

When studying the acid–base equilibria between 4-nitrophenol and triethylamine, we noticed that the relative proportion between the hydrogen-bonded complex and proton-transfer complex (and/or 4-nitrophenoxide) does not depend only on the ratio of [B]/[BH^+] but also on the buffer concentration (Fig. 1).

The increasing buffer concentration at constant ratio of triethylamine to triethylammonium tetrafluoroborate is accompanied by increasing proportion of proton-transfer complex and/or 4-nitrophenoxide. Such behaviour can be explained by different solvation of triethylamine in [bmim][BF_4].

The general equilibrium can be described by Eq. (7).

$$K = \frac{[ArO^-][BH^+]}{[ArOH][B]} \frac{\gamma_{ArO}\gamma_{BH}}{\gamma_{ArOH}\gamma_B} \qquad (7)$$

The formed ions ArO^- and/or BH^+ will be [15b] well solvated in polar ionic liquid, and their activity coefficients will not change much with concentration. Likewise, ArOH will be well solvated [15a], thanks to hydrogen bond basicity of [bmim][BF_4]. In contrast, the very little polar triethylamine will be less well solvated in [bmim][BF_4], and its activity coefficient will increase more steeply with increasing concentration. It can be presumed that the activity coefficient of triethylamine will be much higher than the activity coefficients of other components of the reaction mixture, and its value will be close to those of branched alkanes [20]. A detailed study of relative basicity in systems of amines–phenols will be dealt with in our another communication.

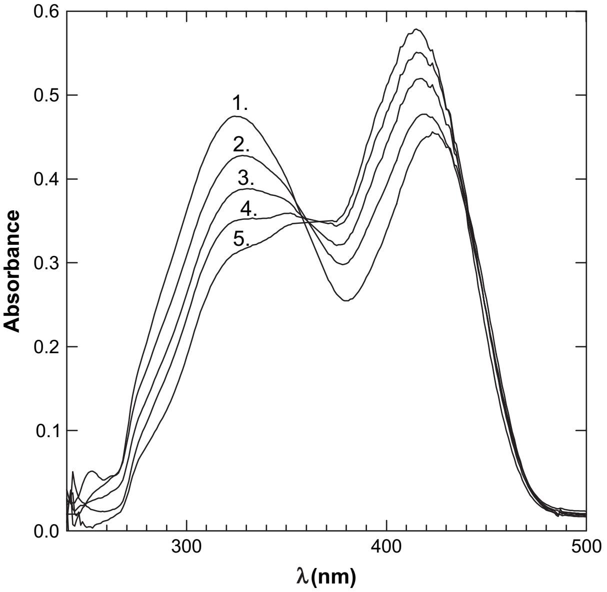


Fig. 1. Spectral records of 4-nitrophenol ($c = 3 \times 10^{-5}$ mol l^{-1}) in solutions of triethylamine buffer at the following concentrations [B] = [BH^+]: 0.01 mol l^{-1} (1.), 0.02 mol l^{-1} (2.), 0.03 mol l^{-1} (3.), 0.04 mol l^{-1} (4.), 0.05 mol l^{-1} (5.).

From Eq. (7) follows that the concentration of [ArO^-] (i.e. concentration of the reactive form in the diazo-coupling reaction) increases with increasing activity coefficient γ_B even at a constant ratio of [B]/[BH^+]. Such increase in concentration of [ArO^-] then accelerates reaction.

3. Conclusions

The study of diazo-coupling reaction by means of kinetic isotope effect ($k_H/k_D = 1$) revealed that the linear increase in observed rate constant (k_{obs}) with increasing triethylamine concentration is not due to operation of general base catalysis. The rate-limiting step is (like in molecular solvents) the formation of the Wheland tetrahedral intermediate, which is supported by the value of reaction constant ($\rho^+ = 1.2 \pm 0.1$). The linear increase in k_{obs} with increasing [B] can be explained by the influence of increasing concentration of [B] upon the activity coefficient γ_B and thereby also upon the position of acid–base equilibrium between the non-reactive 2-naphthol and reactive 2-naphthoxide or its proton-transfer complex (ion-pair). The said effect upon this equilibrium was proved with the cognate 4-nitrophenol by means of spectral measurements. Moreover, it was found that the triethylamine in [bmim][BF_4] possesses a comparable basicity with that of 4-nitrophenoxide ($\Delta pK_a \approx 0$), whereas in water their basicities differ by more than 3.5 orders of magnitude.

4. Experimental

4.1. Kinetic measurements

Kinetic measurements were carried out on an HP UV/VIS 8453 Diode Array apparatus under pseudo-first-order conditions. A 1-cm closeable quartz cell was charged with appropriate amounts (see Table 1) of [bmim][BF_4], stock triethylamine solution in [bmim][BF_4] ($c = 0.1$ mol l^{-1}), stock triethylammonium tetrafluoroborate solution in [bmim][BF_4] ($c = 0.1$ mol l^{-1}) and 20 μl of stock 2-naphthol [bmim][BF_4] solution ($c = 0.05$ mol l^{-1}). This mixture was well shaken and then placed into thermostated compartment. After attaining a temperature of 25 ± 0.1 °C another 20 μl of corresponding benzenediazonium tetrafluoroborate in [bmim][BF_4] solution ($c = 0.004$ mol l^{-1}) was added and after thorough shaking the absorbance—time (A—t) dependence was measured at 480 nm (For example, see Figs. 2 and 3).

The observed pseudo-first-order rate constants k_{obs} were calculated from these dependences with the help of an optimisation program using Eq. (8).

$$A - A_0 = (A_\infty - A_0)\left(1 - e^{k_{obs}t}\right) \tag{8}$$

In all kinetic runs, the standard deviation in the fit was always less than 1.5% of the quoted value, and was more usually between 0.2 and 0.4% of the quoted value. The spectra of products after reaction are identical with that of the products prepared by independent synthesis in the same medium.

4.2. Materials

“Spectroscopic grade” [bmim][BF_4] used for kinetic measurements was prepared from commercially available 1-methylimidazol, 1-chlorobutane (both redistilled under argon before use) and sodium tetrafluoroborate (all chemicals purchased from Sigma—Aldrich). Using known preparative [21] route, it was possible to prepare [bmim][BF_4] that was almost colourless and of sufficient purity and optical clarity to allow study of substances dissolved in them by UV—vis spectroscopy. Water content (0.15% wt) was determined by Karl Fischer titration using METROHM 736 GP TITRINO apparatus.

Triethylamine p.a. (≥99.5%) was purchased from Fluka and used as is. Triethylammonium tetrafluoroborate was prepared from triethylamine according to Ref. [22]. Commercially available 2-naphthol was repeatedly recrystallised from water and dried under vacuum. 1-Deuterio-2-naphthol (91% 1-D) was prepared by a procedure described in Ref. [23] and benzenediazonium tetrafluoroborates **1a—d** were synthesised as reported in Ref. [24].

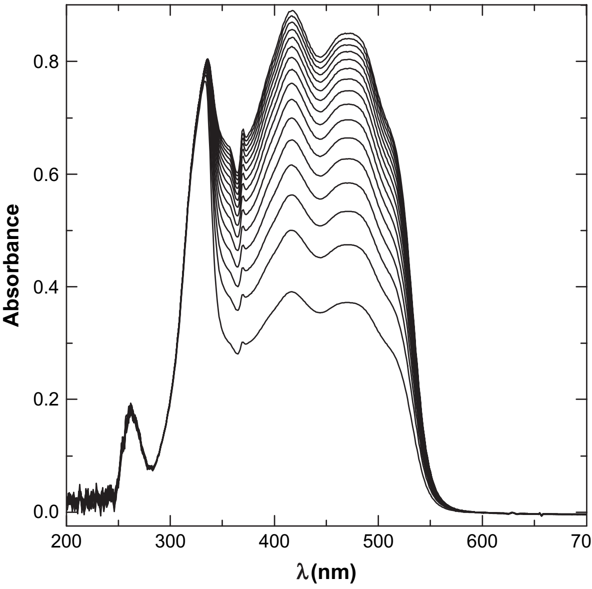


Fig. 2. Spectral record of azo-coupling reaction of 4-methylbenzenediazonium tetrafluoroborate (**1b**) with 2-naphthol in triethylamine/triethylammonium tetrafluoroborate buffer (1:1; $c_{TEA} = 0.02$ mol l^{-1}) in [bmim][BF_4].

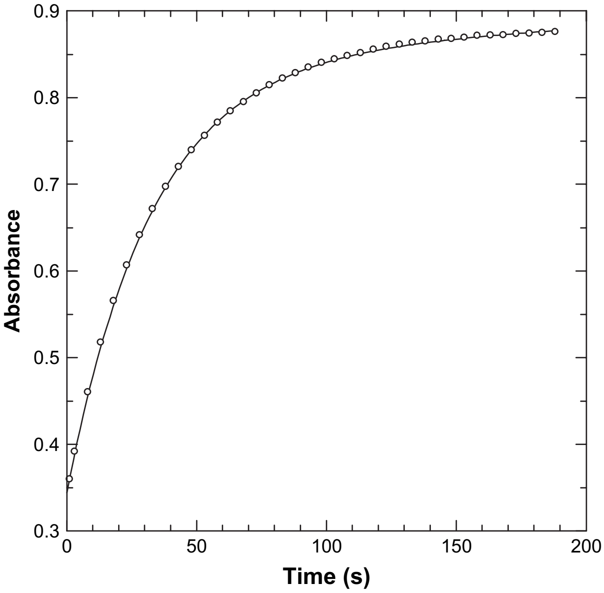


Fig. 3. Measured time dependence of absorbance at $\lambda = 480$ nm (points) and curve calculated using Eq. (1) for kinetic run depicted in Fig. 2.

Acknowledgements

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