Development of a Monitoring Method for Oxidative Coupling Reaction of 2-Naphthol in Solid State

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A monitoring method has been developed for 2-naphthol to 1,1'-bi-2-naphthol conversion reaction. The simultaneous monitoring procedure is based on zero-crossing first derivative spectrophotometry in basic aqueous media. Calibration graphs were obtained for the simultaneous determination. Zero-crossing first derivative wavelengths were 359.7-345.3 nm, respectively for 2-naphthol and 1,1'-bi-2-naphthol determinations. The method showed ability to determine 2-naphthol to 1,1'-bi-2-naphthol ratio 1:15-10:1 (w/w), accurately. Accuracy and reproducibility of the determination method on the known various mixtures of 2-naphthol and 1,1'-bi-2-naphthol were tested in their binary mixtures. The quantitative results of high performance liquid chromatography and analysis of synthetic mixtures (that were prepared according to the compositions obtained by the proposed method) showed satisfactory compatibility with the results of the proposed derivative method.

Key Words: 1,1'-Bi-2-naphthol, 2-Naphthol, Zero-crossing derivative spectrophotometric method, Simultaneous determination, Mechanochemical process.

INTRODUCTION

Mechanochemical processes (MCP) use mechanical energy to activate substances by developing structural changes. The mechanical energy was for the first time pointed out to initiate chemical reactions and local heating is not only the possible mechanism for initiating chemical reactions by mechanical actions[1-7]. Mechanochemistry has been used mostly for inorganic solids. However, application of this method to purely organic reactions has not been well developed before the pioneering and systematic work by Toda and coworkers[8-10].

The solid state reactions which are a branch of solvent free reactions are attractive not only because of the simplicity of the procedure, but also particularly from the view point of environmental protection. Because there is no need for the use of

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harmful organic solvents. Some novel products can be obtained only from solvent-free reactions rather than from the liquid phase reactions. Other advantages of this method are easier workup, shorter reaction time and high yields. Solid state reactions or solvent free reactions are one of the most important synthesis techniques in green chemistry[8-11]. Mechanical milling increases the reaction rates by generating clean and fresh surfaces, increasing defect density and reducing the size of particles[12].

Naphthols are used directly in making several dyes and are converted into numerous corresponding amines, esters, ethers and carboxylic derivatives as well as into numerous sulfo- and nitro-group substituted (mono-, di- and tri-) compounds. It has been found extensive applications in making dyes, pigments, fluorescent whiteners, tanning agents, especially in special medicines, antioxidants and antiseptics. Naphthol structure is found in transition-metal catalysts particularly in the form of 1,1'-bi-2-naphthol which is composed of two naphthol rings connected at one carbon site on each ring[13-17]. Ruthenium-2,2'-*bis*(diphenylphosphino)-1,1'-binaphthyl is used as a catalyst in the production of (R)-1,2-propandiol for the industrial synthesis of levofloxacin. Similar reactions are used for the synthesis of other antibiotics. Noyori's catalysts have found wide application in the synthesis of fine chemicals, pharmaceutical products and new advanced materials[18,19]. Chirally pure 1,1'-bi-2-naphthol is used in the synthesis of enantioselective catalysts for diverse reactions under homogeneous conditions[20-25]. Silica or MCM-41 bonded chiral lanthanum-lithium-binaphthol complexes are used for enantioselective nitroaldol (Henry) reaction in heterogeneous catalysis systems[26,27]. The chiral ligand 1,1'-bi-2-naphthol has been successfully immobilized on polystyrene. Several dendritic and non-dendritic binol derivatives, bearing at least two polymerizable styryl groups, were prepared and fully characterized[28].

It is possible to measure the absolute value of the derivative of the sum curve at an abscissa value (wavelength) corresponding to a zero-crossing of one of the components in the mixture. This is termed a zero-crossing measure and can be applied to the first and the higher order derivatives. The zero-crossing derivative spectroscopic mode allows the resolution of binary mixtures of analytes by recording their derivative spectra at wavelengths at which one of the components exhibits no signal. Zero-crossing measurements for each component of the mixture are therefore the sole function of the concentration of the others[29].

Preparation of some 1,1'-bi-2-naphthols from related 2-naphthols by a mechanochemical vibratory mill is under research. This process has a great importance because of many applications of 1,1'-bi-2-naphthols. The monitoring and reporting of reaction yields need to develop efficient and simple analytical procedures. Based on our knowledge, such procedure has not been developed for monitoring of 2-naphthol and 1,1'-bi-2-naphthol. Therefore, there is a need to develop a procedure for individual determination of 1,1'-bi-2-naphthol or simultaneous determination of 2-naphthol and 1,1'-bi-2-naphthol. This paper reports a simple, accurate and reproducible zero-crossing first derivative spectrophotometric method in basic aqueous

solutions for the simultaneous determination of 2-naphthol and 1,1'-bi-2-naphthol. A reversed phase high performance liquid chromatographic procedure using C_{18} silica bonded phase column was also used to ascertain the proposed derivative method. The simultaneous determination method was tested successfully for monitoring of the coupling reaction of 2-naphthol in a vibratory mill using $FeCl_3$. The proposed method can be used as a simple determination method for studying the mentioned mechanochemical reaction.

EXPERIMENTAL

A Shimadzu 1650 PC scanning spectrophotometer equipped with 10-mm quartz matched cells was used to record the spectra and measurement of the first derivative spectrophotometric responses. The HPLC system consisted of a BFRL model SY-8100 pump with a LC six way-two position valve (Rheodyne, model 7725i), a BFRL UV/vis detector model SY-8200 intelligent UV detector and a Inertex C_{18} (250 mm × 4.6 mm, 5 μm) column. The progress of the reactions was followed by thin layer chromatography (TLC) using silica gel plates (SILIG/UV 254).

The double distilled water, dichloromethane and hydrochloric acid used in this study were analytical grade reagents (Merck). Sodium hydroxide and perchloric acid were prepared from Merck. 1000 μg ml^{-1} of 2-naphthol and 1,1'-bi-2-naphthol (Merck) were prepared in ethanol. Appropriate dilute working solutions of 2-naphthol and 1,1'-bi-2-naphthol were prepared by diluting the appropriate volume of the stock solutions with ethanol (Merck). Water, methanol and ethanol as HPLC grade solvents were prepared from Merck.

Procedure for first derivative spectrophotometric analysis: 2 mL ethanolic solution of samples which contain 2-naphthol and 1,1'-bi-2-naphthol and 1.0 mL sodium hydroxide solution of 2.0 mol L^{-1} were poured into 10.0 mL volumetric flask and the volume was adjusted by adding doubly distilled water. The first derivative spectra of the working solutions were obtained against blank solution in the range 250-400 nm with $\Delta\lambda = 2$ nm using a pair of matched 10.0 mm quartz cells. The first derivative signals were measured at 345.3-359.7 nm for determination of 1,1'-bi-2-naphthol and 2-naphthol, respectively. Concentration of 2-naphthol and 1,1'-bi-2-naphthol were obtained by the related calibration graphs.

Condition for HPLC analysis: The column temperature, injection volume, mobile phase composition, wavelength for UV detector and flow rate of mobile phase were 20 ºC, 20 μL, methanol to water 1:1, 225 nm and 1.0 mL min^{-1}, respectively for the analysis of reaction mixtures by HPLC.

General procedure for oxidative coupling of 2-naphthol under the vibratory mill condition: Different amounts of 2-naphthol and $FeCl_3.6H_2O$ (total amounts less than 2.62 g) in powder form were premixed together and then were transferred into the reactor which was vigorously shaken by the vibratory mill in various conditions. Capsules (with 2.0 cm in diameter and 5.0 cm in length) and balls (with 9.0 mm in diameter) were made of non-abrasive stainless steel. The reactions take place using the apparatus presented in Fig. 1.
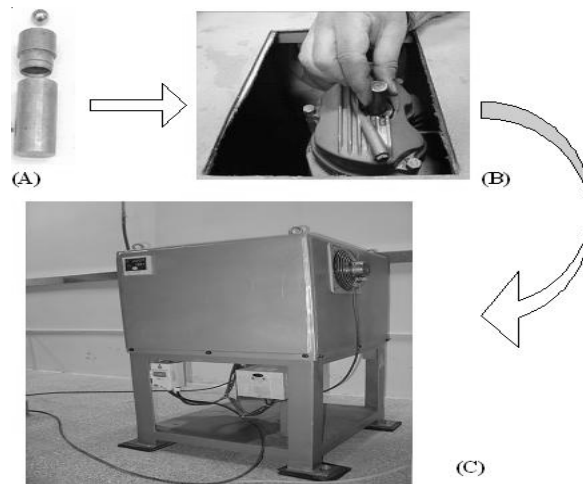
Fig. 1. (A) Reaction chamber and ball, (B) Reactor holder, (C) Vibratory mill device

The reaction mixture was quenched with dilute HCl and extracted into CH_2Cl_2 in a separatory funnel. Then the solvent was evaporated using a vacuum distillator.

RESULTS AND DISCUSSION

Zero and first derivative spectra: In Fig. 2, zero order derivative spectra of 2-naphthol and 1,1'-bi-2-naphthol are observed in basic solutions. The two spectra overlap with each other. Thus zero order derivative spectrophotometry can not be used for determination of 1,1'-bi-2-naphthol at every selected wavelength. To overcome this difficulty, a zero crossing first derivative spectrophotometric procedure may be successful.

By increasing the order of derivative spectrophotometry, minor spectral characteristics are obtainable with better resolutions against the zero order spectra. The first order derivative spectra of 2-naphthol and 1,1'-bi-2-naphthol are shown in Fig. 2. Based on the derivative spectra, two zero-crossing wavelengths for the selective simultaneous determination of 2-naphthol and 1,1'-bi-2-naphthol were observed: 359.7 nm for 2-naphthol determination and 345.3 nm for 1,1'-bi-2-naphthol determination. Therefore the amplitude of the first derivative signal of the 2-naphthol and 1,1'-bi-2-naphthol mixture is proportional to 2-naphthol concentration at 359.7 nm and is independent of 1,1'-bi-2-naphthol concentration also the amplitude of the first derivative signal of the mixture at 345.3 nm is corresponding to 1,1'-bi-2-naphthol concentration and is independent of 2-naphthol concentrations.

Optimization of pH: Initially, in order to optimize the procedure different conditions were tested. The solutions of 2-naphthol and 1,1'-bi-2-naphthol were tested in acidic, neutral and basic solutions and the absorbance spectra of the solutions were recorded against their blanks containing all the reagents except 2-naphthol and 1,1'-bi-2-naphthol. According to the Fig. 3, it can be seen that the spectra of 2-naphthol
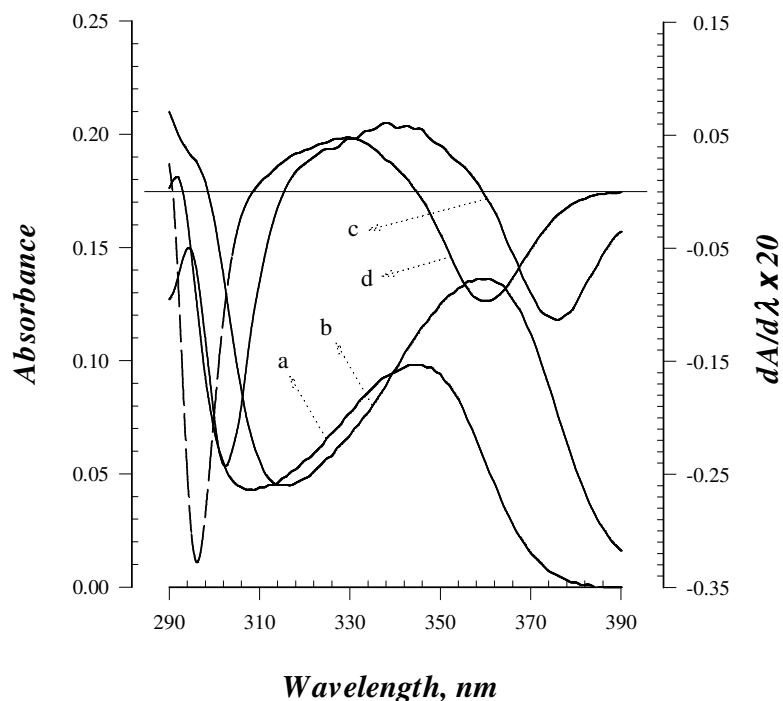
Fig. 2.   Spectra of 2-naphthol and 1,1'-bi-2-naphthol. Absorbance spectra of (a) 2-naph-
thol 5.0 μg mL^{-1}, (b) 1,1'-bi-2-naphthol 5.0 μg mL^{-1}; First derivative spectra of (c)
1,1'-bi-2-naphthol 5.0 μg mL^{-1} and (d) 2-naphthol 5.0 μg mL^{-1} all in 0.20 mol L^{-1}
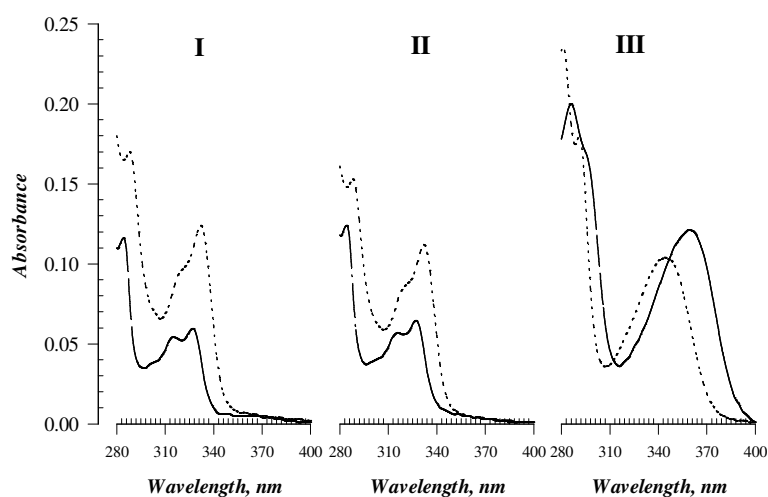sodium hydroxide solutions

Fig. 3.   Absorbance spectra of 2-naphthol and 1,1'-bi-2-naphthol. (I) in water, (II) in 0.20
mol L^{-1} HCl and (III) in 0.20 mol L^{-1} NaOH. (----) 2-naphthol 5.0 μg mL^{-1} and
(—) 1,1'-bi-2-naphthol 5.0 μg mL^{-1}

and 1,1'-bi-2-naphthol are different from each other only in basic media while in the two other media the spectra of 2-naphthol and 1,1'-bi-2-naphthol are nearly the same. Thus basic solution condition was preferred and selected for the further study.

It is necessary that zero-crossing wavelengths do not change by varying concentration of the related species. Zero-crossing method can not be applied for determination of species in which their spectra are shifted. To evaluate the condition, changes in the pre-mentioned zero-crossing wavelengths for 2-naphthol and 1,1'-bi-2-naphthol were tested in the presence of different concentrations of the other species. According to the results given in Fig. 4, no shifts in the zero-crossing wavelengths were observed.
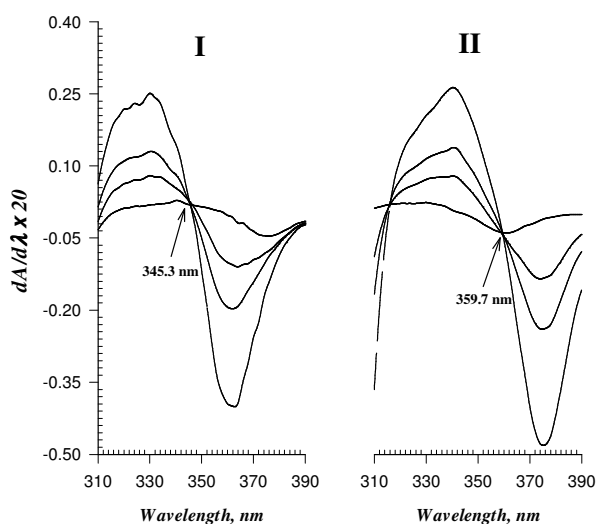

Fig. 4.   First derivative spectra of the solutions as overlays containing: (I) Fixed amount of 1,1'-bi-2-naphthol 2.0 μg mL^{-1} and variable amounts of 2-naphthol 0.0, 5.0, 10.0 and 20.0 μg mL^{-1}, (II) Fixed amount of 2-naphthol 2.0 μg mL^{-1} and variable amounts of 1,1'-bi-2-naphthol 0.0, 5.0, 10.0 and 20.0 μg mL^{-1}, all in 0.20 mol L^{-1} sodium hydroxide solutions

Calibration: Two first order derivative spectrophotometric calibration graphs were constructed; one for 2-naphthol and one for 1,1'-bi-2-naphthol. The obtained calibration parameters have been presented in Table-1.

TABLE-1
CALIBRATION PARAMETERS FOR THE SIMULTANEOUS
DETERMINATION OF 1,1'-BI-2-NAPHTHOL AND 2-NAPHTHOL

Analyte	Calibration equation	Linear range (μg mL^{-1})	Reg.^{2}
2-Naphthol	$dA/d\lambda = 3.1 \times 10^{-5} - 9.60 \times 10^{-4} \times C_{Naph}$	0.5 – 70.0	0.9998
1,1'-bi-2-Naphthol	$dA/d\lambda = -5.3 \times 10^{-5} + 5.80 \times 10^{-4} \times C_{Binaph}$	0.5 – 70.0	0.9991

Condition: 10 mL aqueous solution 0.20 mol L^{-1} sodium hydroxide.

Ten first derivative blank measurements at 359.7-345.3 nm, showed limit of detections about 20 and 15 μg mL^{-1} of 2-naphthol and 1,1'-bi-2-naphthol, respectively ($3 \times S_b$).

Analysis of 2-naphthol and 1,1'-bi-2-naphthol in their binary mixtures: Known different solutions containing 2-naphthol and 1,1'-bi-2-naphthol were analyzed to assess the proposed method. The recoveries and precisions for their simultaneous determinations have been shown in Table-2. According to the results, applicability of the method for simultaneous determination of 2-naphthol and 1,1'-bi-2-naphthol is observed.

TABLE-2
DETERMINATION OF 1,1'-BI-2-NAPHTHOL AND 2-NAPHTHOL
IN SOME OF THEIR BINARY MIXTURES

Sample	1,1'-Bi-2-naphthol (μg mL^{-1})		2-Naphthol (μ mL^{-1})	
	Taken	Found	Taken	Found
1	5.00	5.110 ± 0.14	2.00	2.20 ± 0.080
2[a]	10.00	10.07 ± 0.07	2.00	2.16 ± 0.100
3	2.00	2.00 ± 0.07	20.00	20.3 ± 0.220
4	30.00	30.34 ± 0.82	2.00	2.16 ± 0.070
5	2.00	2.20 ± 0.05	2.00	1.87 ± 0.030
6[b]	2.00	2.22 ± 0.12	5.00	5.27 ± 0.070
7	2.00	1.96 ± 0.12	10.00	10.02 ± 0.120
8	40.00	37.23 ± 0.78	3.00	3.13 ± 0.030
9	10.00	10.07 ± 0.14	10.00	10.10 ± 0.150
10	20.00	19.96 ± 0.07	10.00	10.32 ± 0.110
11	40.00	40.17 ± 0.48	10.00	9.72 ± 0.100
12	10.00	9.88 ± 0.27	20.00	19.93 ± 0.170
13	10.00	10.13 ± 0.15	40.00	40.03 ± 0.170

a: For this sample multiple standard addition method was also used. The results were as follows: 1,1'-bi-2-naphthol 9.87 ± 0.11 μg mL^{-1} and 2-naphthol 2.06 ± 0.09 μg mL^{-1}. b: For this sample multiple standard addition method was also used. The results were as follows: 1,1'-bi-2-naphthol 1.91 ± 0.11 μg mL^{-1} and 2-naphthol 5.10 ± 0.10 μg mL^{-1}. ± Amounts are standard deviation of four replicate analyses.

Validity of the method: Validity evaluation of the proposed first derivative method must be tested. One of the best methods to analysis mixtures is HPLC. HPLC was used as a reference method in this work. Some reaction mixtures were analyzed by HPLC and the obtained results were compared with the results of the proposed first derivative method. The HPLC results confirm the results of the proposed method (Table-3).

Some reaction mixtures were also analyzed by the proposed method. Then according to the obtained results some synthetic mixtures were prepared (from their standard solutions) and their spectra were recorded. The spectra of the reaction mixtures and their synthetic mixtures are presented in Fig. 5. Visual comparison shows no sensible difference between the spectra.

TABLE-3
VALIDITY EVALUATION OF THE PROPOSED METHOD BY HPLC

Sample[a]	HPLC method (%)	Proposed method[b] (%)
1	32.2 ± 2.3	32.8 ± 1.30
2	25.1 ± 0.9	25.5 ± 1.10
3	99.4 ± 0.6	100.9 ± 0.6
4	98.7 ± 0.8	99.1 ± 0.70

a: Conditions: (1) 0.25 g 2-naphthol, 2:1 mol ratio $FeCl_3$ to 2-naphthol, vibration frequency 30 Hz and reaction time 2.0 min; (2) 0.55 g 2-naphthol, 1:1 mol ratio $FeCl_3$ to 2-naphthol, vibration frequency 30 Hz and reaction time 6.0 min; (3) 0.25 g 2-naphthol, 2:1 mol ratio $FeCl_3$ to 2-naphthol, vibration frequency 20 Hz and reaction time 30.0 min; (4) 0.25 g 2-naphthol, 2:1 mol ratio $FeCl_3$ to 2-naphthol, vibration frequency 30 Hz and reaction time 10.0 min. b: Calculated based on produced 1, 1´-bi-2-naphthol. ± Amounts are standard deviation of three replicate analyses (HPLC method) and 4 replicate analyses (proposed method).
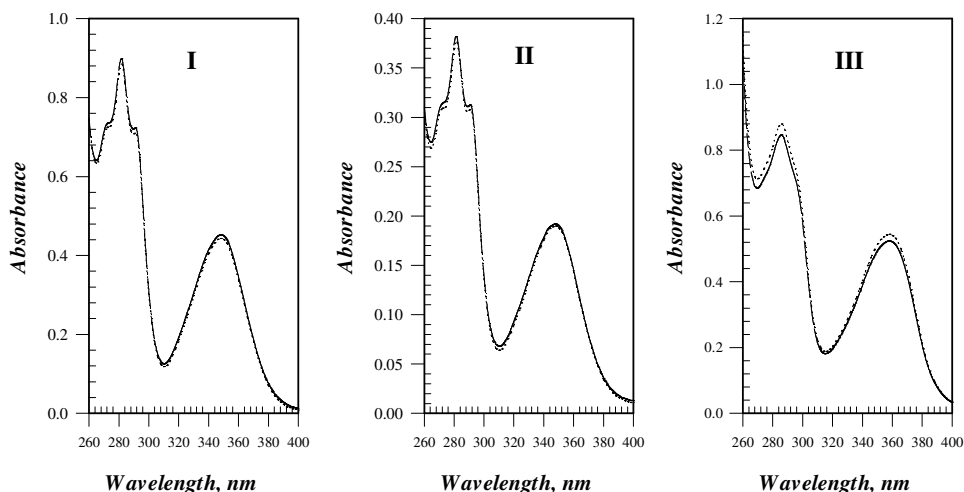

Fig. 5.   Absorbance spectra of some reaction mixtures and their related synthetic mixtures. Condition of reactions: (I) 0.55 g 2-naphthol, 1:1 mol ratio $FeCl_3$ to 2-naphthol, vibration frequency 30 Hz and reaction time 6.0 min, (II) 0.25 g 2-naphthol, 2:1 mol ratio $FeCl_3$ to 2-naphthol, vibration frequency 20 Hz and reaction time 4.0 min, (III) 0.25 g 2-naphthol, 2:1 mol ratio $FeCl_3$ to 2-naphthol, vibration frequency 60 Hz and reaction time 1.5 min. (—) Reaction mixture spectra, (----) synthetic mixture spectra, all in 0.20 mol L^{-1} sodium hydroxide solutions
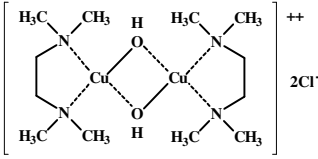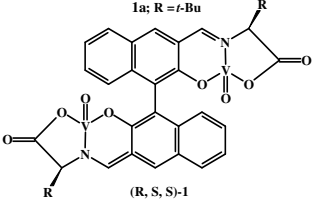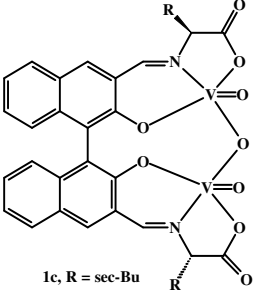
Monitoring of the oxidative coupling reaction in a certain condition has been shown as an example by the proposed method in Fig. 6.

Present reaction shows high efficiency in 1,1'-bi-2-naphthol synthesis. A comparison has been done among some 1,1'-bi-2-naphthol synthesis methods in Table-4.

Conclusion

This study demonstrates the ability of the derivative spectrophotometry for the monitoring of a mechanochemical process. The proposed first derivative method

TABLE-4
COMPARISON OF THE YIELD OF THE SOLID STATE
REACTION WITH THE OTHER METHODS

Author	Catalyst	Solvent	Temp. (°C)	Yield (%)	Reaction time
Nakajima *et al.*[30]	TMEDA + CuCl TMEDA	CH_2Cl_2	RT	81	1 h
Doussot *et al.*[31]	$TiCl_4$	CH_3NO_2	40	90	4.5 h
Hwang *et al.*[32]	$VO(acac)_2$ $(VO(C_5H_7O_2)_2)$	CH_2Cl_2	RT	92	24 h
Somei *et al.*[33]		CH_2Cl_2	30	83	24 h
Guo *et al.*[34]		CCl_4	0	93	6 days
Takemoto *et al.*[35]	*Camellia sinensis* cell culture	H_2O_2	25	47	0.2 h
Ding *et al.*[36]	$FeCl_3$ or NH_4FeCl_4 or $Fe(NO_3)_3$ 'Two phase'	H_2O	50	95	1 h
Prasad *et al.*[37]	Cu-NaMCM-41	C_6H_5Cl	135	97	4.5 h
Bhor *et al.*[38]	K10-FePLS120	H_2O	80	94	3 h
Ikeda *et al.*[39]	V/MCM-41	CH_2Cl_2	30	31.8	24 h
This work[a]	$FeCl_3$	No solvent	RT	95	8 min

[a]Condition of the reaction was 2:1 mol ratio $FeCl_3$ to 2-naphthol (mixture amount 1.19 g), vibration frequency 50 Hz; RT = Room temperature.

not only monitors amount of 1,1'-bi-2-naphthol but also amount of 2-naphthol. Reliability of the simultaneous determination procedure was evaluated by a HPLC procedure. Simplicity, low cost, less time and satisfactory precisions and accuracies are advantages of the proposed method. By this simple procedure, the mentioned solid state reaction will be studied extensively.
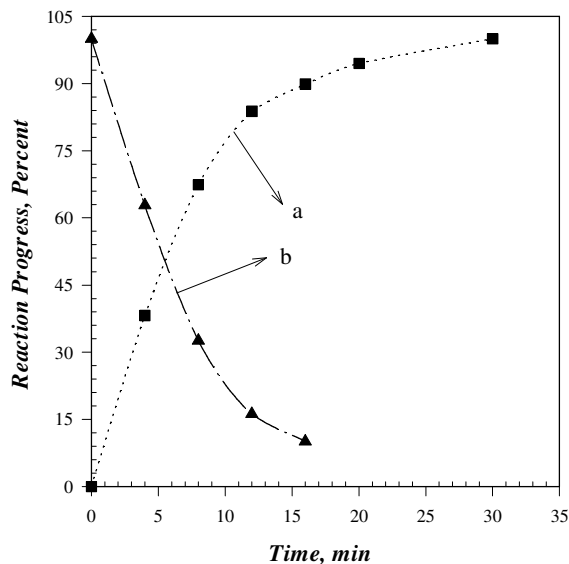
Fig. 6.   Reaction progress (a) 1,1'-bi-2-naphthol percent, (b) 2-naphthol percent. Conditions of reaction: 0.25 g 2-naphthol, 2:1 mol ratio FeCl$_3$ to 2-naphthol, vibration frequency 20 Hz and room temperature

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