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LOGARITHMIC EXTRAPOLATION METHOD FOR KINETIC DETERMINATION OF AMINE MIXTURES

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ABSTRACT. A kinetic method for the simultaneous determination of binary mixtures of aromatic amines and of β-naphtol and 1-phenyl-3-methylpyrazolin-5-one by logarithmic extrapolation is reported. The method involves the formation of an azo dye between coupling agent and a diazonium salt formed from the amine in the presence of nitrite in weak acidic media. The reaction is monitored spectrophotometrically by the formation of an azodye absorbing at 420 nm.

Keywords: kinetic methods, para-toluidine, azodye

INTRODUCTION

The method is based on the equation describing the modification of absorbance under pseudo-first order conditions.

Total concentration of analiyte is determinated from total concentration of products or via initial rate. The relative errors were in the range of 0.5 to 6% for the most cases.

The logarithmic extrapolation method is the most commonly used graphical linear method for the simultaneous kinetic determination of two species in a mixture. The method has been used in analytical chemistry for the determination of mixture of organic species[1-3] or heavy metal ions[4-6].

This method features several advantages, namely[7]:

-no prior knowledge of the rate constant of the analytes is necessary;

-it is less prone to error as the linear plot is constructed from several points;

-rate constant ratios as low as five are acceptable under certain condition.

The purpose of the present study is to use the logarithmic extrapolation method for the determination of *para*-toluidine and aniline in mixture and of β-naphtol and 1-phenyl-3-methylpyrazolin-5-one, respectively. Indicator reaction is of a Bratton-Marshall type, the formation of an azodye.

Despite of the great variety of methods reported, the Bratton-Marshall procedure is still the most widely used for the determination of sulphonamides in clinical work[8,9]. Bratton-Marshall method is based on transformation of the free primary aromatic amine into a diazonium salt by means of nitrous acid; the diazonium salt is rapidly coupled with a chromogenic reagent such as *N*-(1-napthyl)ethylenediamine[10]. It is also known that the semiquinone radicals derived by partial oxidation of aromatic *p*-diamines have intense color and react with various aromatic amines and phenols to give intensely colored indamine and indoaniline dyes. The increase of absorbance can be used to indicate the reaction advancement and consequently the reaction rate[11, 12].

In this work, indicator reaction is a coupling one between benzenediazonium salts (***1***) formed *in situ* (proceeding from aniline and/or *para*-toluidine) and 1-phenyl-3-methylpyrazolin-5-one (***2***) or β-naphthol (***3***) with HNO_2.

The kinetics of the reaction has been previously investigated. The reaction obeyed a rate law of first-order in each, diazonium salt and coupling agent, and the effect of the acidity is known[12].

EXPERIMENTAL

All reagents but coupling agent were of analytical-reagent grade and solutions were prepared in de-ionized and four-distilled water or reagent grade ethanol. 1-phenyl-3-methylpyrazolin-5-one (***2***) was prepared in our laboratory as previously described[13] and purified by re-crystallization from ethanol. Stock solution (1×10^{-3} M) was prepared in ethanol. Sodium nitrite (1 M) and (***2***) (5×10^{-3} M) solution were prepared in de-ionized water and ethanol respectively. A 4.6×10^{-3} M perchloric acid solution was also used to generate the hydrogen ion as requing.

Kinetic measurements have been performed spectrophotometrically by means of a JASCO V-530 spectrophotometer. It has an automatic data linked acquisition to a computer. Temperature was controlled at 20 ± 0.1^0C by means of a LAUDA M 12 temperature - controlled bath connected to the cell holder.

The reaction was followed at an appropriate wavelength (420 nm) of the dye formed by coupling reaction. 1.0 mL of standard aromatic amine solution, 0.5 mL of (***2***) 5×10^{-3} M and 0.5 mL of perchloric acid 4.6×10^{-3} M were placed in a 5 cm path length cuveette and accurately diluted to 11.5 mL. The reaction was initiated by rapid addition and thoroughly mixing of 0.25 mL solution of sodium nitrite 1 M over 11.5 mL of other reactants mixture. It was previously kept in the temperature bath for at least 15 min. The progress of the reaction was monitored and kinetic data (absorbance *vs.* time) were collected and processed by computer. The initial rate was measured after the induction period, within the domain of linear dependence (about 300 s). Each sample was repeated for at least three times for the same set of experimental conditions. Replicate run data yielded the same results within the error limits of 0.5 %.

RESULTS AND DISCUSSION

Para-toluidine or aniline in weakly acidic solutions react with nitrious acid to yield a diazonium salt. In the presence of 1-phenyl-3-methylpyrazolin-5-one (***2***) or β-naphthol (***3***), diazonium salt forms azo dyes (***4***) and (***5***) by a quite rapid coupling reaction respectvely. The reactions are present in figure 1.

An attempt has been made to determine either a mixture of two aromatic amines or a mixture of 1-phenyl-3-methylpyrazolin-5-one and β-naphthol using para-toluidinediazonium salt.

The method is based on the equation describing the modification of absorbance under pseudo-first order conditions. Therefore under the large excess of one reactant:

$$\frac{A_\infty - A}{A_\infty - A_0} = \frac{[A]_0}{[A]_0 + [B]_0} \cdot e^{-k_1 \cdot t} + \frac{[B]_0}{[A]_0 + [B]_0} \cdot e^{-k_2 \cdot t} \qquad (1)$$

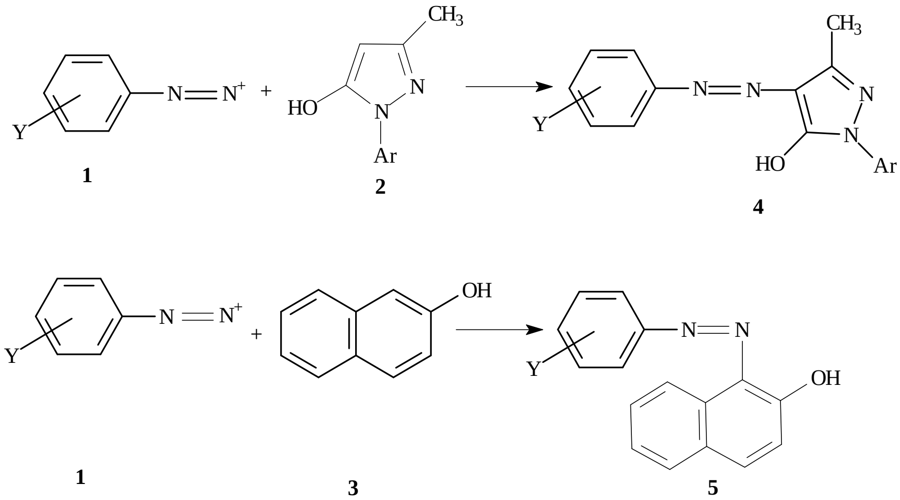

Figure 1. *Indicator reaction (Y = H or CH_3)*

Providing that $k_1 > 5\ k_2$, towards the end of the process, the reaction of 1-phenyl-3-methylpyrazolin-5-one (***2***) with anilinediazonium salt has been accomplished and the first exponential term gets vanished. It means that, within this period of time, only the reaction of 1-phenyl-3-methylpyrazolin-5-one (***2***) and *para*-toluidinediazonium ion (k_2) take place. The rapid process (k_1) has been already accomplished. Thus:

$$\ln\frac{A_\infty - A}{A_\infty - A_0} = \ln\frac{[B]_0}{[A]_0 + [B]_0} - k_2 \cdot t \qquad (2)$$

By plotting $\ln\frac{A_\infty - A}{A_\infty - A_0}$ versus t a straight line should be obtained. The rate constant k_2 is the slope of the line and $\ln\frac{[B]_0}{[A]_0 + [B]_0}$ (the fraction of *para*-toluidine in the initial mixture) as the intercept can be obtained. Figure 2 presents this kind of plot.

By using these values and transforming equation (1) into a form containing known amounts in the left side, the following is obtained:

$$\ln\left(\frac{A_\infty - A}{A_\infty - A_0} - \frac{[B]_0}{[A]_0 + [B]_0} \cdot e^{-k_2 \cdot t}\right) = \ln\left[\frac{[A]_0}{[A]_0 + [B]_0}\right] - k_1 \cdot t \qquad (3)$$

By plotting left side of equation (3) as a function of time (figure 2), using experimental date obtained at the beginning of the kinetic measurement, the ratio of aniline can be determined from the intercept of the line.

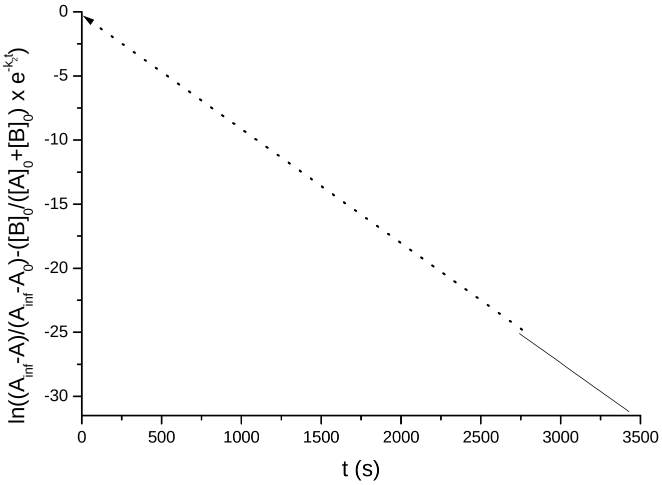

Figure 2. *Determination the ratio of para-toluidine*

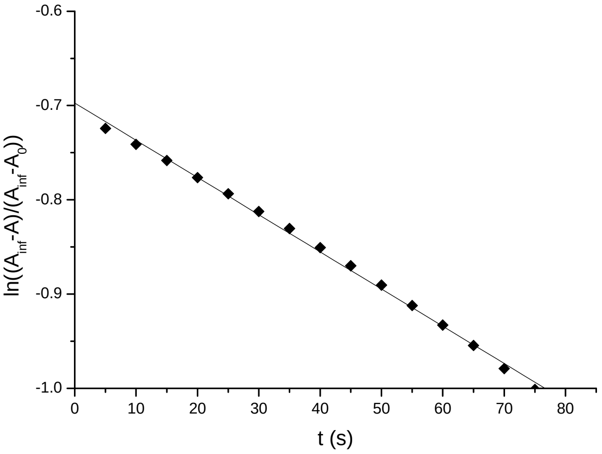

Figure 3. *Determination the ratio of 1-phenyl-3-methylpyrazolin-5-one*

Table 1.

The prediction for some mixtures of *para*-toluidine and aniline

Analyte Ratio	Analyte fraction				Relative errors %	
	addend	found				
	p-toluidine	aniline	*p*-toluidine	aniline	*p*-toluidine	aniline
1:1	50.0	50.0	50.1	49.8	0.2	-0.4
1:2	33.3	66.6	31.4	66.9	-5.7	0.5
2:1	66.6	33.3	65.8	32.3	-1.2	-3.0
1:4	25.0	75.0	23.8	74.8	-4.8	-0.3
4:1	75.0	25.0	73.0	24.1	-2.7	-3.6
1:5	20.0	80.0	19.8	81.7	-1.0	2.1
5:1	80.0	20.0	83.6	18.8	4.5	-6.0

Table 2.

The prediction for some mixtures of β-naphthol and 1-phenyl-3-methylpyrazolin-5-one

Analyte Ratio	Analyte fraction (%)				Relative errors (%)	
	addend	found				
	β-naphtol	Phenil-pyrazolone	β-naphtol	Phenil-pyrazolone	β-naphtol	Phenil-pyrazolone
1:1	50.0	50.0	50.2	49.7	+0.40	-0.60
1:2	33.3	66.6	31.6	66.5	-5.11	-0.15
2:1	66.6	33.3	65.7	32.8	-1.35	-1.50
1:4	25.0	75.0	24.0	75.4	-4.00	+0.53
4:1	75.0	25.0	72.0	25.3	-4.00	+1.20
1:5	20.0	80.0	19.5	82.1	-2.50	+2.63
5:1	80.0	20.0	81.7	18.5	2.13	-5.50

A similar method[14] was used for the determination of 1-phenyl-3-methylpyrazolin-5-one and β-naphtol in mixture. The indicator reaction was the coupling reaction between bezenediazonium salts and 1-phenyl-3-methylpyrazolin-5-one or β-naphtol. In this case the prediction for some mixtures is presented in Table 2. Total concentration of analyte is determinated from total concentration of products or via initial rate[15].

Several measurements were performed in the presence of various concentrations of metal ions usually present in rivers or wastewaters such as Cu^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, and Pb^{2+}. The concentration up to 8.5×10^{-4} M were used that exceeded common concentration of these ions in waters. No effect on the initial rate has been noticed.

CONCLUSIONS

The method permit to determine mixture of para-toluidine with aniline and mixture of 1-phenyl-3-methylpyrazolin-5-one with β-naphthol.

Relative errors are quite good ranging between the limit 0.5 - 6.0 %.

The usual metal ions frequently present in water do not interfere with the measurement.

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