

Double Peak Phenomena In Flow Injection Analysis Using PAR-KMnO₄ Reaction

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Abstract

The main aim of this study is to investigate the double peaks which were observed by the reaction of PAR as a reagent with KMnO₄, in order to understand the phenomena of the double peak observation in flow injection analysis technique to prevent this phenomena and to get the single and sensitive optimization for determination and identification with good detection limit.

To resolve whether the double peaks result of physical or chemical optimization, or both. The results proved that the phenomena of double peak observed in the both cases of physical, and chemical effects.

By optimizing the optimum conditions of experiments in condition of forming double peaks were observed and found that.

In physical phenomena, the possibility of double peak is quite possible in short reaction coil, and high flow rate. In chemical phenomena the possibility of double peak is quite possible in the formation of different complex species by the effect of different pH.

Introduction:

In some 4-(2-pyridylazo)-resorcinol (PAR) reactions with KMnO₄, the double peaks were observed. This phenomena was investigated to resolve whether the double peaks were risen as a result of physical or chemical effect, or both.

The phenomena is observed using FIA technique. The same phenomena was observed, in some pyrocatechol violet reactions with bismuth ^[1].

There are two principal prospects of FIA. The first is in the automation of conventional batch procedures based on peak height measurement, the second involves taking advantage of the highly reproducible and manipulable dispersion profile of an injected sample plug.

The physical phenomena, which cover some dispersion in FIA are, flow rate, tube diameter, length of tube over which the reactions takes place, and sample volume ^[2].

Between the points of injection and detection, the sample plug will have been physically dispersed to some degree, and in addition some chemical reactions may take place.

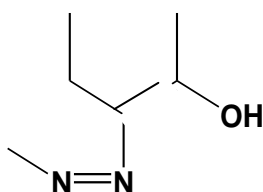
The physical dispersion is brought partly by longitudinal flow rate, and partly by radical diffusion. The former is favoured by short coil length, and fast flow rate, and results in a sharp symmetrical peak shape in FIA, whilst latter is more important with long coil length, and slow flow rate, and gives rise to symmetrical Gaussian shaped peaks.

In physical phenomena, the possibility of double peak is quite possible in short reaction coil, and high flow rate.

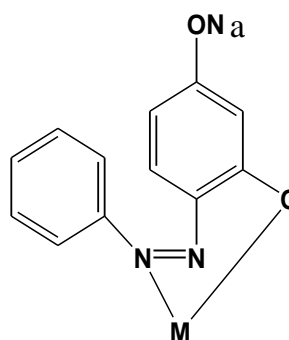
In chemical phenomena, the possibility of double peak is quite possible in, chemical species, and in the pH selection ^[3].

PAR, and its chemistry as a complex agent:

PAR, is a polyprotic, and is used as an acid base indicators, it is characterized by the configuration of its chromophoric group:



Which participates in the chelate formation with metal ion, e.g.: - Cu, Ca, Mn of intensely coloured complexes.



PAR has three dissociation constants, the most acidic H₃In being at pK_a = 2.3, whilst H₂In is at pK_a = 6.95 and HIn at pK_a = 12.4 ^[4].

Experimental

1- Reagents:

Standard Samples:

KMnO₄: Stock solution of 10⁻²M was prepared from potassium permanganate (BDH), and diluted to give a solution from 5x10⁻⁴ – 5x10⁻⁵M.

Carrier Solution:

PAR: Aqueous solution of PAR from (Aldrich) of 5x10⁻³ M was prepared.

Buffer solutions:

Bellow pH 2 the pH solution was controlled by addition of nitric acid, pH 2-5 standard phthalate buffer was used, pH 6-8 standard potassium dihydrogen phosphate with sodium hydroxide was used, and above pH 9 controlled by addition of sodium hydroxide.

2- Apparatus:

Fig. (1) is a schematic diagram showing the apparatus used.

- A Dosage (W. Germany No. 833294) multi-purpose peristaltic pump was used, which provided a constant flow rate.

- A Rotary valve was used, were the samples injected into reagent stream.

- Polyethylene tubing of 0.86 mm i.d was used for various coils of the system.
- Spectrophotometer (Philips-P48620 UV/Vis/NiR] was used as a detector.
- pH-meter with combined electrode.
- Flow cell.
- Chart recorder-Model- connected to the spectrophotometer to record the output.

3- Procedure

As in Fig. (1) the carrier flow rate was adjusted to require flow rates as in Table (1) for different effects, and aliquots of 0.3 ml for coil reaction effect, 0.25 ml for pH effect and different volume sample for flow rate effect were injected into carrier stream.

The absorbance of resultant and coloured complexes were mentioned on a chart recorder.

Results

Some experimental works were held. The FIA system was optimized to find the best conditions under which the multiple peaks were arose. To investigate the physical effect on the formation of the double peaks in the PAR/KMnO₄ reactions:-

Effect of flow rate

Effect of decreasing and increasing the flow rate can be seen in Fig. (2), under the optimum condition as in Table (1).

By increasing the flow rate the double peaks were formed as a single peak and losing their shoulders which is resolved when the flow rates were decreased.

Effect of coil length

Effect of increasing and decreasing the coil length can be seen in Fig. (3) under the optimum condition as in Table (1).

By increasing the coil length the double peaks were formed, and the double peaks were resolved by decreasing the coil length.

The possible explanations to this phenomenon in a coil length and flow rate, that may be the physical effect resulting from incomplete mixing of sample and reagent. So reagent depletion occurs near the center of the sample plug. Hence the double peaks are due to sample and reagent reaction of these interfaces.

Investigation into contribution from chemical effect on the double peak.

Effect of pH:

The experiments of PAR with KMnO₄ were held at pH 7 which is the pK_a for PAR, and therefore the equilibrium of two species was established, the KMnO₄ it could react with either species:

The effect of pH on the appearance of double peak was investigated.

Below pH 6 it was noted that the precipitation occurred in the tubing after a sample of KMnO₄ had been injected into the buffer PAR.

Therefore, only pH values around H₂In and HIn were investigated.

Fig. (4) shows the effect of pH on the shape of record peaks with coil length (coil reaction) of 1.56 meter. It can be noted that the double (and even triple peaks at pH 6) exist around H₂In, which are replaced with single peaks under more basic conditions at the third pK_a (basic) only one peak was recorded. Some experiments were held by changing both flow rate, and coil length, under same selective pHs for complex formation, the phenomena of double peaks remains, only at pH 6, these peaks were obtained which were combined into two peaks at the larger coil length, the larger coil length represents a longer time interval before the sample reaches the detector and hence a longer time of reaction.

Conclusion

In general there are two possibilities of double peaks phenomena formation in FIA system; the physical effect, and chemical effect, the phenomena can be explained in both cases.

In chemical phenomenon the pH has a great effect on the formation of double peaks; the double peaks remain by changing the physical conditions of the experiments.

The double peaks also may be observed by the effect of pK_a; in each pK_a there are two different species, which they have different molecular diffusion^[6].

In physical phenomenon the possibility of double peak is quite possible in a short reaction coil length, and high flow rate, which both effect on mixing between sample plug and carrier, with short time there is no proper mixing, thus for the formation of double peak is quite possible due to reaction of the sample carrier interface and unreacted part in the center of the sample plug (sample depletion).

On the other hand as physical phenomena, the sample concentration has a great effect also in the shape of peak formation, at low concentration proper mixing, single peak forming, and with high concentration sample depletion forming, which cause double peaks as mentioned before.

In the result the formation of the double peak is quite possible by both chemical and physical effect.

Chemical effect is a pH selective of reaction, and physical effect is a proper mixing which is caused by sample concentrations, coil length, and flow rate. The method is quite suitable to be used for the determination of KMnO₄ as a sensitive and accurate technique by FIA in a condition to choose both physical and chemical optimization which prevent the formation of double peaks.

Table (1) Optimum conditions for the formations of the double peaks

Effect of the on the peak height	Parameter	Conditions
Coil Reaction	Sample	5×10^{-4} M KMnO_4
	Reagent	5×10^{-3} M PAR
	Sample volume	0.3 ml
	Tube Length (cm)	a)172, b)259, c)356 and d) 456
	Flow Rate	1.2 ml/min.
	pH	7
pH	Sample	5×10^{-4} M KMnO_4
	Reagent	5×10^{-3} M PAR
	Sample volume	0.25 ml
	Tube Length	156 cm
	Flow Rate	1.2 ml/min.
	pH	6,6.5,7,7.4,8 and 9
Flow Rate	Sample	5×10^{-4} M KMnO_4
	Reagent	5×10^{-3} M PAR
	Sample volume(ml)	a and b 0.15, c,d,e,and f 0.3
	Tube Length (cm)	a and b 172, c,d,e, and f 356
	Flow Rate ml/min.	a1.2, b0.37, c1.5, d2.1, e3.2,and f 9.2
	pH	7

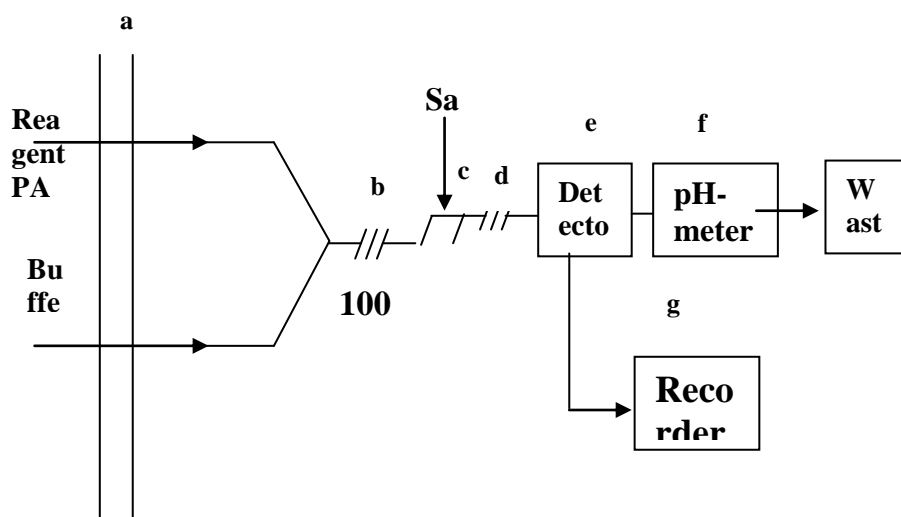


Fig. (1): Schematic diagram of apparatus for reaction of PAR and KMnO_4

a- peristaltic pump, b-mixing coil, c- injection valve, d- reaction coil
e- spectrophotometer, f- pH-meter, g-chart recorder

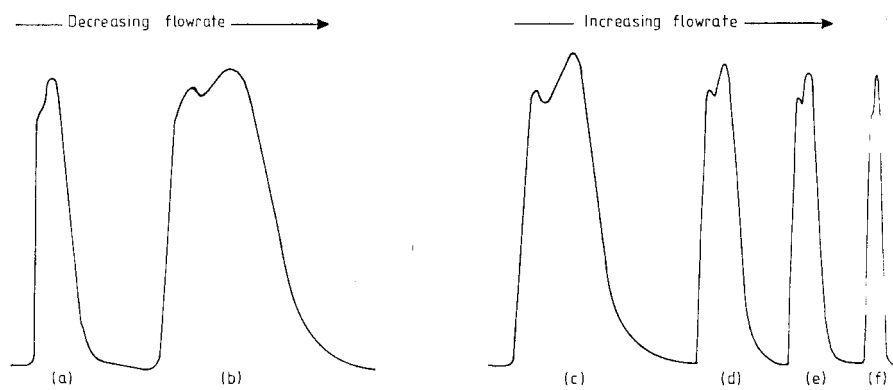


Fig. (2): Effect of flow rate on the peak shape

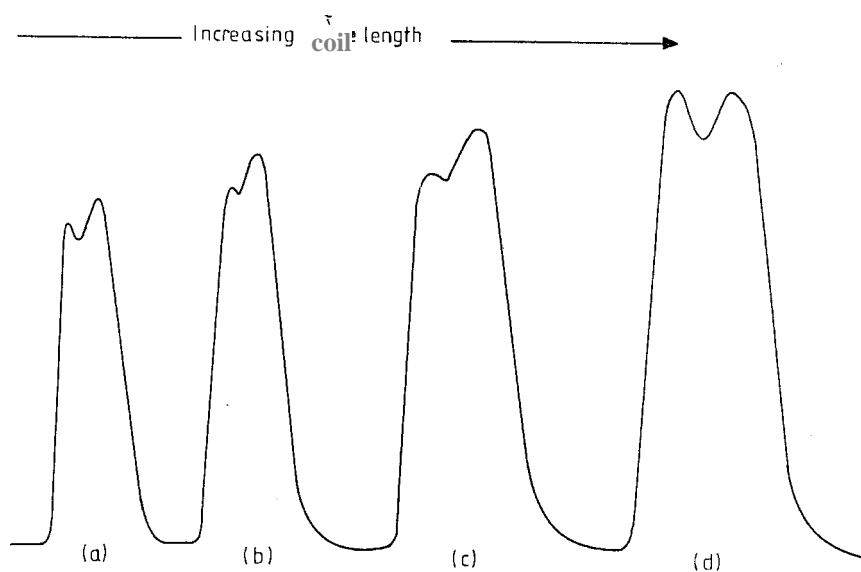


Fig. (3): Effect of coil reaction on the peak shape

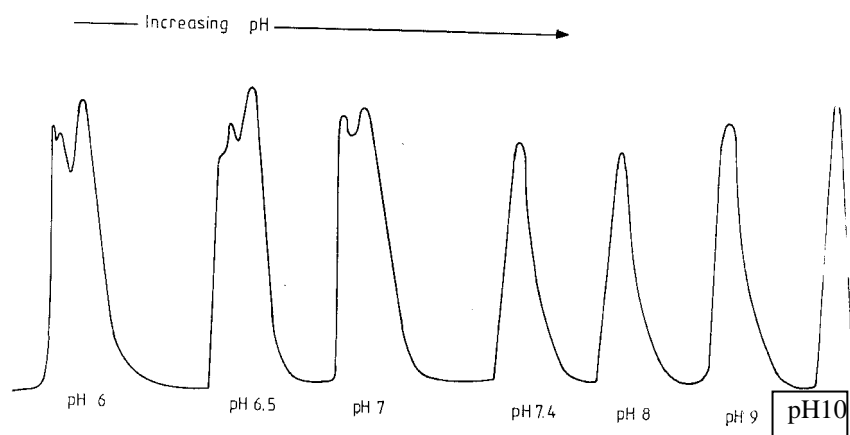


Fig. (4): Effect of pH on the peak shape

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