

A NEW ACID BASE INDICATOR

Its pK_a and pT Values

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Abstract. 2-nitroresorcinol has been used as an acid-base indicator. In acid it is yellow while in basic form it changes to red colour. The pH range of the indicator is 5.4 to 7.4. The pK_{in} is 6.4 ± 0.1 and pT value is 6.2. As pK_{in} 6.4 is reasonably near to 7.0, which is the equivalence point pH of strong acids versus strong bases, therefore, it is more suitable than the commonly employed indicators, phenolphthalein and methyl orange which have pK_{in} 8.3 and 4.2 respectively.

The synthesis of 2-nitroresorcinol was described by Kaufmann and Depay¹, Carpenter,² and Lofgren and Takman³, which was then modified and simplified by Schaffrath.⁴ This reagent can be very easily prepared in the laboratory. We have found that this compound can be used as an acid base indicator. In acid medium the colour of this compound is yellow and in basic medium it changes to red. The famous indicators, methyl orange and methyl red are little difficult to synthesize, but 2-nitroresorcinol can be easily prepared in the general laboratory and used for acid base titrations. Its pH range has been investigated and pK_{in} has also been found. Its pK_{in} is 6.4 which is near to pH 7, the equivalence point pH of strong acids versus strong alkalies. It is more suitable than phenolphthalein and methyl orange which have pK_{in} 8.3 and 4.2 respectively. The major drawback of phenolphthalein is that it can not be used for the titrations where carbon dioxide is present while 2-nitroresorcinol is not effected by the presence of carbon dioxide.⁵ Therefore, it can be employed when sodium carbonate is being titrated.

Experimental

Reagents

All the reagents used were of analytical grade or of comparable purity.

2-nitroresorcinol 0.01M solution was prepared in 95% ethanol.

Phenolphthalein 0.02M solution was prepared by dissolving it in 50 ml alcohol and then diluting it with 50 ml water. 0.1M solution of sodium hydroxide, sodium carbonate, hydrochloric acid and 0.2M solution of sulphuric acid were prepared in distilled water.

pH Solutions. Various pH solutions ranging from 1-11 were prepared from different single substances⁶ to avoid salt effect and pH was measured by pH meter. Before measuring pH of the solutions the pH meter was standardized carefully using buffer solutions ranging 1-11 pH.

Equipment

Microburette of 5 ml capacity, graduated at 0.02 ml. All absorbance measurements were made with Bechman DB-spectrophotometer using 1 cm cells. Pye Dynacap pH meter was used for pH measurements.

Procedure

Acid-base Titration. An accurately measured volume of the alkali solution was placed in a 25 ml. Erlenmeyer flask and to this were added four drops of 2-nitroresorcinol as indicator. The alkali solution was then titrated against standard acid from a microburette. The end point was reached when slight excess of the acid changed the colour of the solution from red to yellow.

Absorption Characteristics of 2-Nitroresorcinol. A 0.01M solution of the indicator was prepared and its absorption spectrum was taken in the visible range. The absorption maximum was at 370 nm. The absorption maximum of the indicator in 0.1M HCl was at 330 nm and it shifted to 440 nm in 0.1M Na_2CO_3 solution.

pH Range of the Indicator. 11 measuring flask of 25 ml capacity were taken and to each was added an equal amount of indicator say 0.2 ml and the volume was made upto the mark with different pH solutions. The absorption of each solution was then measured at 440 nm.

pK_a of the Indicator. pK_{in} of the indicator can be calculated from values of absorbance determined against each pH range by applying the following equation:

$$pH = pK_a + \log \frac{I_{NB}}{I_{NA}} + \log \frac{f_{INB}}{f_{INA}}$$

Where pH will be the pH range of the indicator. I_{NA} and I_{NB} are the concentrations of the acidic and basic forms of indicator respectively, at a certain pH and were found from the spectral data because the concentrations are directly proportional to absorbance f_{INA} and f_{INB} are the activity coeff

ponents of the acidic and basic forms respectively of the indicator and these are taken as unity because the concentrations are quite low.

The actual absorbance of the acid and basic forms of the indicator were calculated by applying the following relationship :

$$A_a = A_{Mb} - A_p$$

$$A_b = A_p - A_{Ma}$$

Where A_a , A_b and A_p are the absorbances of the acidic, basic and sample solution of the indicator respectively at 440 nm at a certain pH. A_{Ma} and A_{Mb} are the maximum absorbances of the indicator in 0.1M HCl and at pH 9.0 respectively.

pT Value of the Indicator. Titration exponent (pT) is the concentration of hydrogen ion at which the sharpest change in the colour of the indicator takes place during titration and it enables oneself to use the indicator where it is most suited. The pT value should be as close as possible to the pH value of the equivalence point. The pT value should be in the middle of the transition range and was found by graphic method.

Results and Discussion

It is clear from Tables 1-3 that the 2-nitroresorcinol can be successfully used for the titration of strong alkalies against strong acids. The indicator error is also negligible in the titration of sodium carbonate with hydrochloric acid. The well known indicator phenolphthalein cannot be used in this titration⁷ because carbon dioxide which comes out of this reaction interferes with the end point of phenolphthalein. Neutral red will be the best indicator to be used, but 2-nitroresorcinol is also ideal because its pK_{in} and pT values are 6.4 and 6.2 respectively which are quite near to the pH of the equivalence point of the above mentioned titration.

It can be visualized from the curve in Fig 1 that the pH range of the indicator is 5.4 to 7.4 ± 0.1 pH units and the pK_a value is 6.2 ± 0.1 . The pK_a of the indicator was also calculated from the equation given in procedure. It was found to be 6.4 which is the average of various values ranging from pH 5.4 to 7.4. Both values of pK_a 6.4 and 6.2 are in quite good agreement.

TABLE 1. DETERMINATION OF SODIUM HYDROXIDE WITH HYDROCHLORIC ACID USING 2-NITRORESORCINOL AS INDICATOR.

NaOH taken (mg)	NaOH found (mg)	Standard deviation
1.72	1.72	0.01
3.45	3.43	0.05
4.92	4.95	0.05
6.43	6.46	0.06
8.18	8.13	0.01

Every result is the average of 5 determinations.

TABLE 2. DETERMINATION OF SODIUM CARBONATE WITH HYDROCHLORIC ACID USING 2-NITRORESORCINOL AS INDICATOR.

Na ₂ CO ₃ taken (mg)	Na ₂ CO ₃ found (mg)	Standard deviation
4.48	4.49	0.03
6.65	6.64	0.01
7.06	7.04	0.04
11.77	11.79	0.06
26.28	26.27	0.01

Every result is the average of 5 determinations.

TABLE 3. DETERMINATION OF SODIUM HYDROXIDE WITH SULFAMIC ACID USING 2-NITRORESORCINOL AS INDICATOR.

NaOH taken (mg)	NaOH found (mg)	Standard deviation
0.24	0.24	0.02
0.972	0.975	0.01
1.77	1.77	0.01
3.39	3.40	0.05

Every result is the average of 5 determinations.

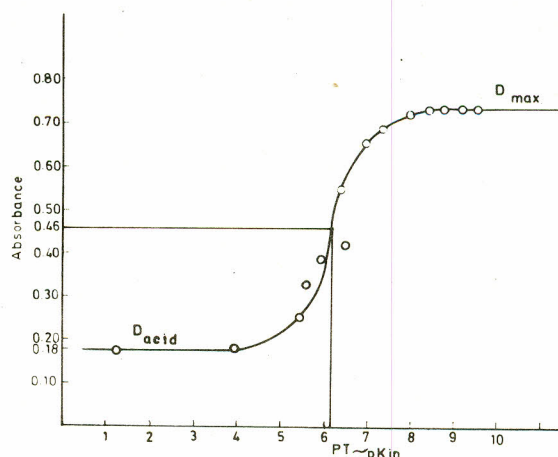


Fig. 1. pH range of 2-Nitroresorcinol (absorption maximum at 440 m μ).

The pT value was estimated from Fig. 1 and it was also 6.2 which is approximately equal to pK_a . This value of pT indicates that it can be used in these acid-base titrations where equivalence point pH is near to this value.

This indicator was used in titrations of Tables 1-3 because the equivalence point pH in these cases is 7.0. The pT value 6.2 is quite near to 7.0 as compared to other conventional indicators like methyl orange, methyl red and phenolphthalein which have pT values 4.0, 5.0 and 9.0 respectively.

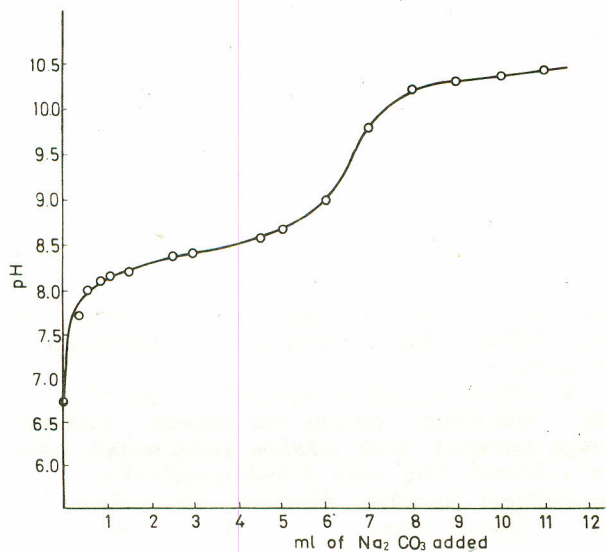
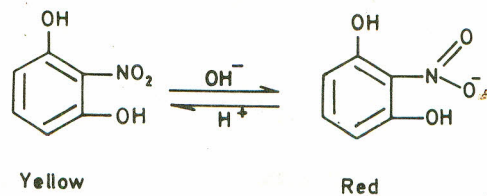


Fig. 2. Titration curve of 10 ml of 0.01M 2-Nitroresorcinol with 0.01M Na₂CO₃.

In order to know whether monoanion or dianion of nitroresorcinol was responsible for the colour change of the indicator in the pH titration of 0.01M 2-nitroresorcinol against 0.01M Na₂CO₃ Fig. 2 was drawn and the curve shows that only one proton is involved in the titration and second proton cannot

be removed by 0.01M Na₂CO₃ and the colour change can be shown as follows:



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