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Short Communication

pH-Titrimetric method for the estimation of isomeric xylidines and triethylamine

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Abstract

A pH-titrimetric method is described for the determination of triethylamine and isomeric xylidines. Neutral salts NaCl and NaI are employed to obtain sharp end points in methanol–water semiaqueous medium. Reproducibility of determinations at about 99 per cent purity has been found to be ± 1·88% for triethylamine and ± 0·88% for xylidine.

Key words : pH-metric titration, isomeric xylidine, estimation.

1. Introduction

Aliphatic amines are relatively strong bases and give sharp breaks in titration curves in aqueous media. However, no such sharp end points are obtained with weakly basic aromatic amines rendering accurate analysis very difficult. It has been pointed out that neutral salts when present in solution, enhance the potentiometric break for the titration of weak bases with aqueous mineral acids[1, 2]. We applied the idea for the determination of triethylamine and isomeric xylidines (i-XDA) formed during catalytic hydrogenation of nitroxylene. A methanol-water semiaqueous media was chosen for titration. Methanol is required to cause dissolution of i-XDA. Sodium chloride and sodium iodide were employed as neutral salts to enhance the potentiometric break. Sodium iodide is strongly soluble in water. 6 M NaI solution is easily made in methanol–water mixture.

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2. Materials and methods

Reagent-grade methanol, sodium chloride, sodium iodide and triethylamine were used. Standard HCl solution of accurately known strength (~ 0·5 N) was used for titration. A Naina-make digital pH-meter with an accuracy of ± 0·01 pH units was used.

2.1 *Estimation of triethylamine*

Extra care is needed to prevent any loss of the sample during sampling as well as titration due to the highly volatile nature of TEA. 5–6 g of sodium chloride or 44–45 g of sodium iodide is weighed in a 100 ml capacity titration vessel fitted with ground glass stopper. 30 ml of distilled water is added and contents shaken well to make a clear solution followed by the addition of 20 ml of methanol. In case NaI is used it is advisable to add methanol first followed by distilled water. The titration vessel with solution is cooled in a freezing mixture.

The sample is precooled in ice-bath or a refrigerator. 0·5–1·5 g of precooled sample is drawn into a syringe and transferred to 2–3 ml capacity preweighed glass ampoule with its neck drawn into a capillary. The ampoule neck is sealed and again weighed. Sample weight is found from the difference of the two weights. The ampoule is dropped into the precooled titration vessel containing methanol–water–NaCl (or NaI) solution. The ampoule is broken into the solution by means of a glass rod. The glass rod is washed with a small quantity of water and rinsings allowed to drop into the solution. The titration vessel is immediately closed by means of GG stopper and shaken gently to dissolve the sample.

2.2 *Estimation of xylidines*

In the case of i-XDA, about 0·2 to 1·2 g of sample is taken. Rest of the procedure is the same as above. The i-XDA amount being large, more methanol may have to be added to cause complete dissolution and make a clear solution. However, it is important to note that the amount of methanol added should be just sufficient to cause dissolution of xylidine. Excess methanol is to be avoided to prevent electrode noise. Extra precaution of cooling recommended for TGA need not be followed.

In both the cases, the titration vessel is removed to a magnetic stirrer assembly and a teflon-coated bar magnet is dropped into the solution. A combined pH-electrode is inserted through a hole in a rubber stopper and the nozzle of a 50-ml burette through another hole in the rubberstopper which fits on the top of the titration vessel to make it airtight. The bulb of the glass electrode dips into the solution. Standard HCl solution is dropped through the burette and pH (mv) read from pH-meter. The solution is continuously stirred during titration. The pH (mv) is plotted against HCl volume added and the end point computed from the peak in dpH/dmv derivative-volume curve. As expected for triethylamine, an aliphatic amine, a sharp break in titration curve occurs

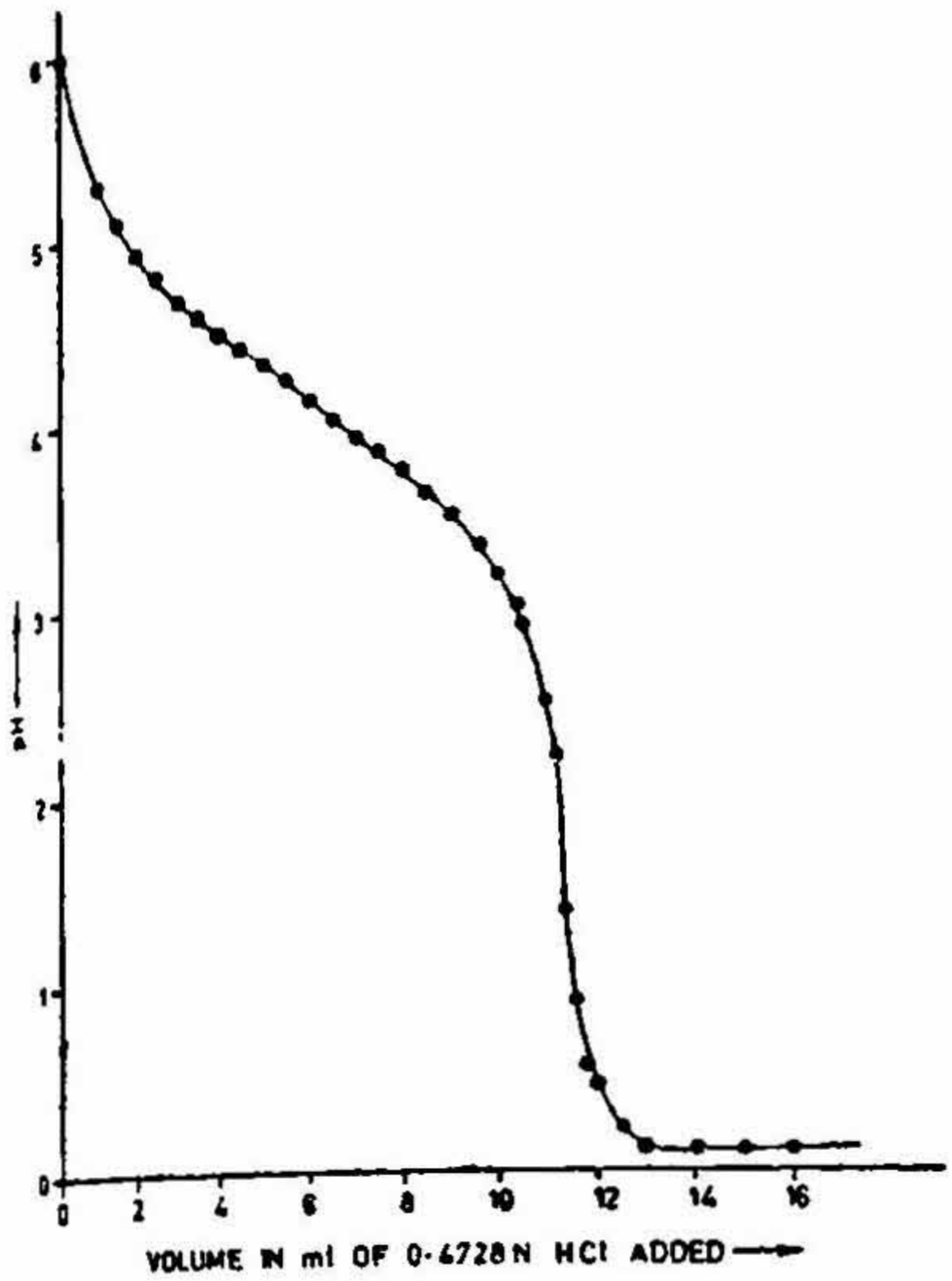

FIG. 1. pH-metric titration of 0·6594 g xylidine + 20 ml methanol made up to 50 ml in 6 M NaI against 0·4728 N HCl.

between pH range 1·25 and 9·0, where the change of pH with the slightest addition of HCl is extremely sharp. In xylidine the sharp pH change occurs between pH range 0·5 and 3·5 (fig. 1), where the addition of HCl is to be very accurately controlled.

The amount of amine present in the sample is calculated from the following relationship:

$$\% \text{ of amine (by weight)} = \frac{0{\cdot}1\text{M} \times \text{Normality of HCl solution} \times \text{Volume of HCl (in ml)}}{\text{Sample weight (in g)}}$$

where, M is the molecular weight of the amine, it being 101·19 and 121·18 for TEA and i-XDA respectively.

With the precautions followed, we feel that the results are reproducible within the following limits for the assay of nearly pure TEA and isomeric xylidines :

Triethylamine	$\pm$ 1·88 % ($n = 6$)
Xylidine	$\pm$ 0·88 % ($n = 9$)

where n is the number of analyses made.

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