POTENTIOMETRIC TITRATION OF P-ANISIDINE AND P-TOLUIDINE IN NON-AQUEOUS MEDIA

Sevgi Kocaoba*, Feray Aydogan, Huseyin Afsar

Yildiz Technical University, Faculty of Art & Science, Department of Chemistry, Davutpaşa Cad. No:127, 34210- Davutpasa, İstanbul, Turkey.

ABSTRACT

Potentiometric titrations of p-anisidine and p-toluidine were carried out with hydrochloric acid in toluene solvent. The same titrations were done with hydrochloric acid in methanol solvent to show the effect of amphiprotic solvent in the titrations with hydrochloric acid. For each weak base, an S-shaped potentiometric titration curve was obtained. As a result, toluene, which is an aprotic inert solvent, is a suitable solvent for titrating some of the weak bases potentiometrically.

Keywords: non-aqueous titrations, toluen, hydrochloric acid, p-anisidine, p-toluidine

INTRODUCTION

Titrations in non-aqueous solvents have been traditionally an important tool for the accurate determination of various pharmaceuticals, some acids in foods, use of some acids or bases in detergents, cosmetics and textile auxiliaries, in the analysis of industrial process streams, the analysis of polymers /1-7/. The determination of the pK_a or pK_b values of organic compounds with acidity or basicity constant less than 10^{-8} can only be realised in non-aqueous media. Although water has excellent solvent

*Corresponding author: Sevgi Kocaoba. Tel: +90 212 449 1637, Fax: +90 212 449 1514, e.mail: kocaoba@yildiz.edu.tr

properties, it is not suitable for such organic compounds since the pH jump at the equivalence point in aqueous solution cannot be evaluated with reasonable accuracy, with this result, the end point cannot be found. Moreover, most of this compounds are not soluble in water. For these reasons, titration in non-aqueous media has recently acquired great importance. It is now well known that non-aqueous titrations greatly depend on the solvents used /4, 8-13/.

Many weak bases can be determined titrimetrically. However, titration of this weak bases in aqueous solution will be neither accurate nor precise because the end-points generated from weak bases are not significant /14/. Generally, $HClO_4$ is used as a titrant for determination of weak bases in non-aqueous media. However, commercial $HClO_4$ contains 28-30 % water corresponding to approximately $HClO_4.2H_2O$. Anhydrous $HClO_4$ titrant is prepared by dissolving the aqueous $HClO_4$ in acetic acid or in sulfolane and then adding enough acetic anhydride to react with all the water. When combined with $HClO_4$, weak acid, acetic acid shows strong acid effect at the end point of the titration. Furthermore, acetic anhydride contained in titrant may interfere by reacting with some easily acetylatable amines to generate corresponding acetylated product, which do not consume acid. To eliminate the problems mentioned above with $HClO_4$, we used HCl as a strong acidic titrant in non-aqueous titration of weak bases, p-toluidine (pK_b: 8.92) and p-anisidine (pK_b: 8.66). Although very weak bases cannot be quantitatively determined, when amphiprotic solvents are used in neutralisation titrations, there are very few research and published papers focusing on titration in aprotic solvents. These are mainly on titrations having benzene, which is highly carcinogenic, as solvent. So toluene, which is an aprotic inert solvent, was chosen in non-aqueous titration with HCl. The major advantage of inert solvents is that they do not compete for protons with the reactant in a titration; that is, these solvents have autoprotolysis constants approaching zero. Thus, neutralisation reactions should be more nearly complete when carried out in solvents of this type. The primary disadvantage of these solvents is that most acids and bases tend to be sparingly soluble in them but this disadvantage can be eliminated by using small volumes of amphiprotic solvents together with inert solvents. The small amounts of amphiprotic solvents do not effect the competition of weak bases with solvent in proton transfer. Because the amount of aprotic solvents is much less, competition between weak bases and amphiprotic solvents in proton transfer can be done easily.

EXPERIMENTAL

Chemicals

p-Toluidine, p-anisidine, toluene, methanol, calcium chloride, potassium chloride, calcium oxide were purchased from Merck, sulphuric acid and sodium chloride were technical grade. p-Toluidine and p-anisidine were used after recrystallisation from ethanol-water mixture. Toluene was dried by distillation from metallic sodium. Methanol was dried by refluxing with calcium oxide, which dried in the furnace for 5 hours at 600 °C, for 6 hours followed by distillation from calcium oxide.

For the preparation of standard hydrochloric acid solution concentrated sulphuric acid was added drop wise from dropping funnel to solid sodium chloride in a two necked flask, which carried a spray trap. The hydrogen chloride evolved was absorbed in dry toluene after drying with concentrated sulphuric acid in a wash bottle. The amount of absorbed hydrochloric acid by toluene was determined by mixing of known volume of prepared hydrochloric acid with deionised water to transfer hydrochloric acid into water, then titration with decimolar sodium hydroxide solution. 0.1 M HCl solution used as titrant was prepared by dilution of this solution with water free toluene. The hydrochloric acid solution in methanol was prepared same way using water free methanol instead of toluene.

Standard 0.02 M p-toluidine and p-anisidine solutions were prepared by dissolving corresponding amounts (2 mmol) of amines in water free toluene containing 5 % dry methanol (100 ml) and methanol separately. Methanol was used for development solubility of amines in toluene.

Apparatus

Metrohm Herisau Prazisions-pH meter E 510 and combined electrode were used for the potentiometric titrations and the electrode was filled with saturated solution of potassium chloride in water free methanol instead of aqueous potassium chloride.

The potentiometric titrations were performed in a three necked vessel equipped with electrode, drying tube filled with calcium chloride, semi-microburette and a magnetic stirrer. The burette had an adaptor which connected with a drying tube and the 0.12 M HCl solution bottle, and filled with the solution by means of nitrogen gas flow dried over calcium chloride.

Titrations were carried out at room temperature. The volume of amine solution titrated was 50 ml and this was magnetically stirred during the addition of titrant. The titrant was added in 0.5 ml quantities. After each addition of titrant, approximately one minute was allowed before measurements were made to reach ionic equilibrium.

RESULTS AND DISCUSSION

Titration curves of the weak bases, p- toluidine and p- anisidine with HCl in toluene (0.12 M) solvent are given in Figures 1 and 2. The same titrations were also carried out with HCl in methanol solvent to show the effect of amphiprotic solvent in the titrations with HCl. The results are given in Figures 3 and 4.

The shapes of the titration curves indicate that toluene is an excellent solvent for these weak bases. From the interpretations of the data, the following results were deduced.

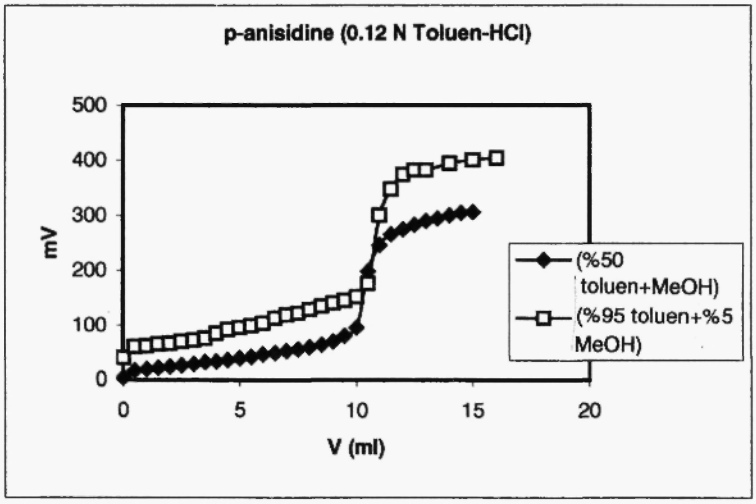

Fig. 1: Potentiometric titration curve of p-anisidine with HCl in toluene solvent

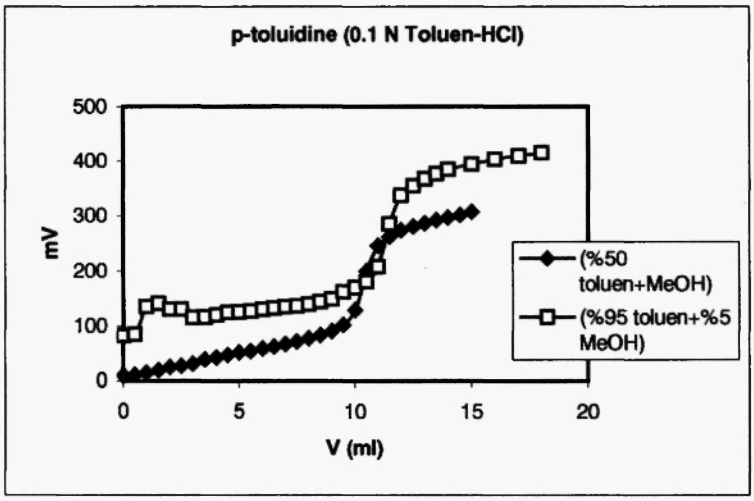

Fig. 2: Potentiometric titration curve of p-toluidine with HCl in toluene solvent

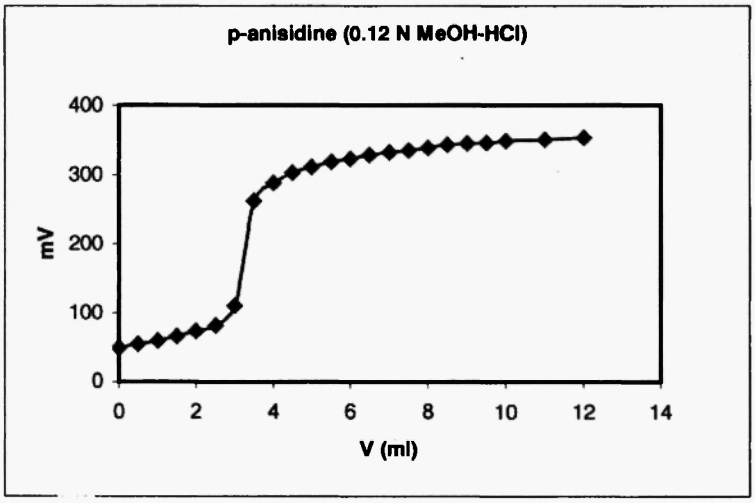

Fig. 3: Potentiometric titration curve of p-anisidine with HCl in methanol solvent

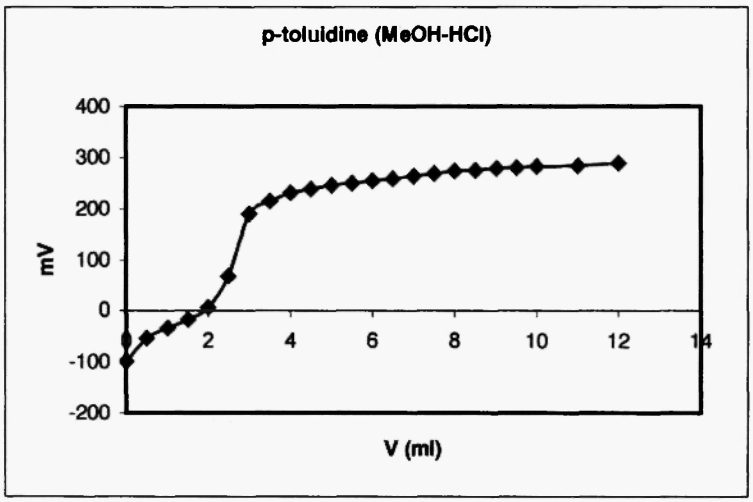

Fig. 4: Potentiometric titration curve of p-toluidine with HCl in methanol solvent

Titration curves, produced plotting the exchange of electrode potential difference against to titrant, of the p-toluidine and p-anisidine solved in toluene: MeOH (methanol) (95:5) mixture, with HCl in toluene solvent (0.12 M) are given in Figures 1 and 2. Titration of these weak bases with HCl in toluene gave well defined and stochiometric end-points as a large potential break occurred at the equivalence points. The recovery percentage of the titrated substances were calculated as 99.0 % and 101.4 % respectively for p-anisidine and p-toluidine.

The same weak bases also titrated with HCl in methanol solvents to show the effect of amphiprotic solvent in the titration with HCl. The titration curves are given in the Figure 3 and 4. Interestingly, these titrations had different potential change in the curves, but these changes do not show the complete neutralization points of bases. For example, from the titration curve of 2 mmol p-anisidine (AND), it was found that the end point was equal to 0.38 mmol acid. This situation can be interpreted to reaction of CH_3O^- ion which is present in the medium from the following reaction (Eq.1) with H^+ ion (Eq.2).

$$CH_3OH + AND \rightleftharpoons CH_3O^- + ANDH^+ \quad (1)$$

$$CH_3O^- + H^+ \rightleftharpoons CH_3OH \quad (2)$$

The end-point may be seen because of the low reaction rate of Equation 1. Indeed, the acid amount (0.34 mmol) calculated from the end-point in Figure 4 is smaller than that of Figure 3 (0.38 mmol), since the stronger base p-anisidine (pK_b: 8.66) has more CH_3O^- ions in the equilibrium than p-toluidine (pK_b: 8.92).

To support this interpretation, titrations of methanol and methanol: water (98:2) mixture without base were carried out with HCl in methanol. pH versus V and mV versus V graphics are given in Figures 5 and 6. Only a fast pH decrease was observed because of the neutralization of CH_3O^- ions which are found in the medium according to Equation 3

$$2\,CH_3OH \rightleftharpoons CH_3O^- + CH_3OH_2^+ \quad (3)$$

as can be seen in Figure 5 - graphic 1. A small amount of water was added to the media to see the effect of water. When water was added into the media more pH decrease was observed (Figure 5- graphic 2) than graphic 1 as a result of neutralisation of OH^- ions from the autoprotolysis of water which has higher autoprotolysis constant than MeOH. Titrations carried out in non-aqueous media with a very small amount of alcohol, which can be autoprotolysed, definitely show only one end-point which is equal to weak bases (Figures 1 and 2). As the amount of methanol decreases in the medium, the pH change increases and the acid consumption decreases at the end-point. Thus, as the amount of methanol increases, the pH change is observed at small amounts of acid consumption. In Figure 6 fast mV increase was observed as expected and this increase was a bit higher than titration of methanol: water mixture.

As a result, inert and aprotic solvent toluene is suitable for the titration of weak bases in non-aqueous media as solvent, although benzene which is more carcinogenic aromatic hydrocarbon used widely in literature for non-aqueous titrations. The major advantage of toluene is that it does not compete for protons with the reactant in the titrations because of its autoprotolysis constant approaching zero. The major disadvantages of solubility can be removed by using small amount of amphiprotic solvents.

HCl is also a good titrant for weak bases because of its great solubility in

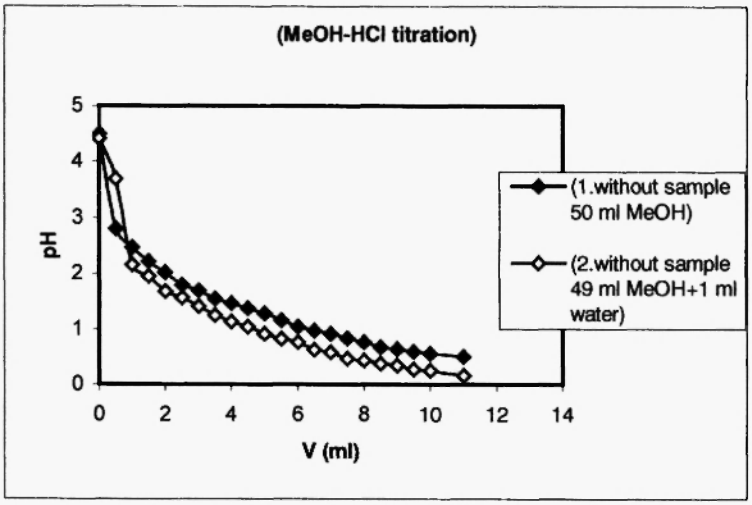

Fig. 5: pH- V curve for MeOH-HCl titration without sample

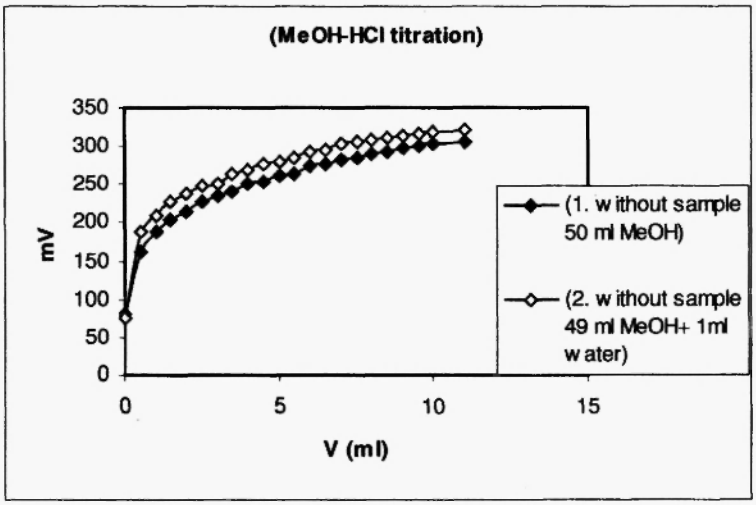

Fig. 6: mV- V curve for MeOH-HCl titration without sample

most solvents; i.e. 0.58 N in toluene and 0.86 N in MeOH at saturation point and availability from cheap compounds such as NaCl and H_2SO_4.

The method used for non-aqueous titrations of weak bases is also easily applicable and convenient method in every laboratory.

REFERENCES

1. M. Bos and W.E. Linden, *Anal. Chim. Acta*, **332**, 201 (1996).
2. E. Kılıc, F. Koseoglu, A. Kenar and M.A. Akay, *J. Pharmaceut. Biomed. Anal.*, **13**, 1453 (1995).
3. A.H. Aktas, G. Yasar, G.O. Alsancak and S. Demirci, *Turk. J. Chem.*, **25**, 501 (2001).
4. M. Yalcin, S. Tanyolac, I. Kizilcikli and A. Tavman, *Turk. J. Chem.*, **22**, 155 (1998).
5. R.H.Q. Vyas and R.B. Kharat, *Ind. J. Pharm. Sci.*, **50**(5), 279 (1988).
6. J. Urbanski, K. Czerwinski, F. Janicka, H. Majewska and H. Zowall, *Handbook of Analysis of Synthetic Polymers and Plastics*, Ellis Horwood, Chichester, 1977.
7. T. Gunduz, G. Ozkan and B. Gunduz, *Microchim. Acta*, **126**(3-4), 227 (1997).
8. T. Gunduz, N. Gunduz and M. Hayvalı, *Anal. Chim. Acta*, **78**(2), 243 (1993).
9. T. Gunduz, E. Kılıc, G. Ozkan, M. Awaad and M. Tastekin, *Anal. Chim. Acta*, **234**(2), 339 (1990).
10. T. Gunduz, E. Kılıc and O. Cakırer, *Talanta*, **43**(5), 771 (1996).
11. O. Cakırer, T. Gunduz and E. Kılıc, *Ind. J. Chem. A*, **37**(11), 1032 (1998).
12. J. Glinski, G. Chavepeyer and J.K. Platten, *Chem. Physics*, **272**, 119 (2001).
13. E. Kaczmarczyk and L. Chmurzynski, *J. Molec. Struc.*, **526**, 41 (2000).
14. X.S. Qui, R.B. Miller, Y. Namiki, Z. Zhang and R. Jacobus, *J. Pharmaceut. Biomed. Anal.*, **16**, 413 (1997).