NON AQUEOUS TITRATIONS: POTENTIOMETRIC TITRATION OF SOME PRIMARY AMINES

Sevgi Kocaoba*, Feray Aydogan, Huseyin Afsar

Yildiz Technical University, Faculty of Art & Science,
Department of Chemistry, Davutpaşa Cad. No:127,
34210- Davutpasa, Istanbul, Turkey.
e.mail: kocaoba@yildiz.edu.tr

ABSTRACT

Potentiometric titrations of some primary amines; 1-aminobutane, 1-aminopropane and 3-amino-1-phenylbutane 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.

Key words: non-aqueous titrations, toluen, hydrochloric acid, 1-aminobutane, 1-amino propane, 3-amino-1-phenylbutane

INTRODUCTION

Potentiometric titrations in non-aqueous media yield valuable information about the basicity and acidity of compounds /1-2/. Titrations in non-aqueous solvents have been traditionally an important tool for the accurate

* Corresponding author: Sevgi Kocaoba.
Tel: +90 212 383 4145, Fax: +90 212 383 4106,
e.mail: kocaoba@yildiz.edu.tr

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 /3-9/. 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 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 these compounds are not soluble in water. For these reasons, titration in non-aqueous media has recently acquired great importance. Solvent effects are particularly important; in many cases, the basicity of a molecule varies when the solvent is changed /6,10-16/.

Many weak bases can be determined titrimetrically. However, titration of these weak bases in aqueous solution will be neither accurate nor precise because the end-points generated from weak bases are not significant /17/. HCl was used as a strong acidic titrant in non-aqueous titration of 1-aminobutane, 1-amino propane and 3-amino-1-phenylbutane. As a part of our research on non-aqueous titrations of some weak bases in toluene, we obtained good results /18/. Although very weak bases cannot be quantitatively determined, when amphiprotic solvents are used in neutralisation titrations, there are very limited numbers of 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, as 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 a small volume of amphiprotic solvents together with inert solvents. The small amounts of amphiprotic solvents do not affect 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

1-aminobutane, 1-aminopropane and 3-amino-1-phenylbutane, toluene, methanol, calcium chloride, potassium chloride, calcium oxide were purchased from Merck; sulphuric acid and sodium chloride were technical grade. 1-aminobutane, 1-amino propane and 3-amino-1-phenylbutane were used without further purification. 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, then followed by distillation from calcium oxide for 6 hours.

For the preparation of standard hydrochloric acid solution, concentrated sulphuric acid was added dropwise from a 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 hydrochloric acid absorbed by toluene was determined by mixing a 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 the same way using water free methanol instead of toluene.

Standard 0.02 M 1-aminobutane, 1-aminopropane and 3-amino-1-phenylbutane 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 developing 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 0.15 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 measurement was made to reach ionic equilibrium.

RESULTS AND DISCUSSION

The titration curves of 1-aminobutane, 1-aminopropane and 3-amino-1-phenylbutane with HCl in toluene (0.1 M) solvent are given in Figures 1-2. 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 3-4.

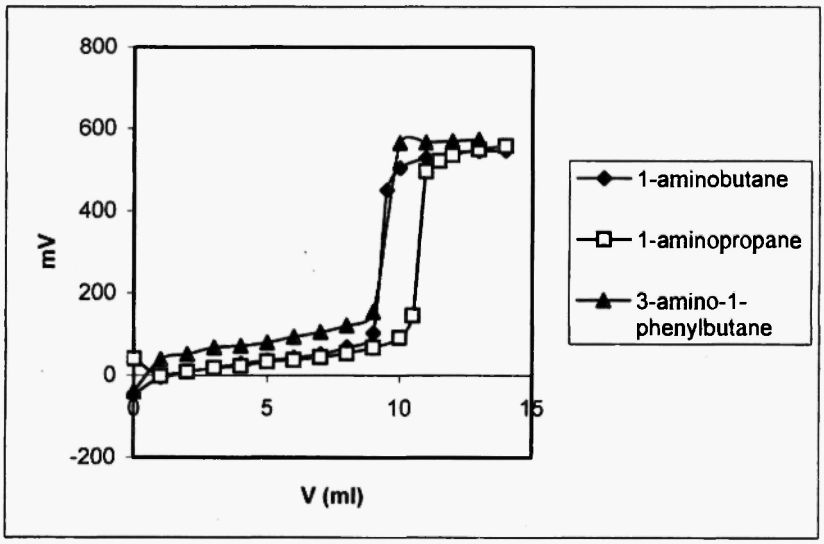

Fig. 1: Potentiometric titration curve of primary amines with HCl in toluene solvent (mV-V graphic)

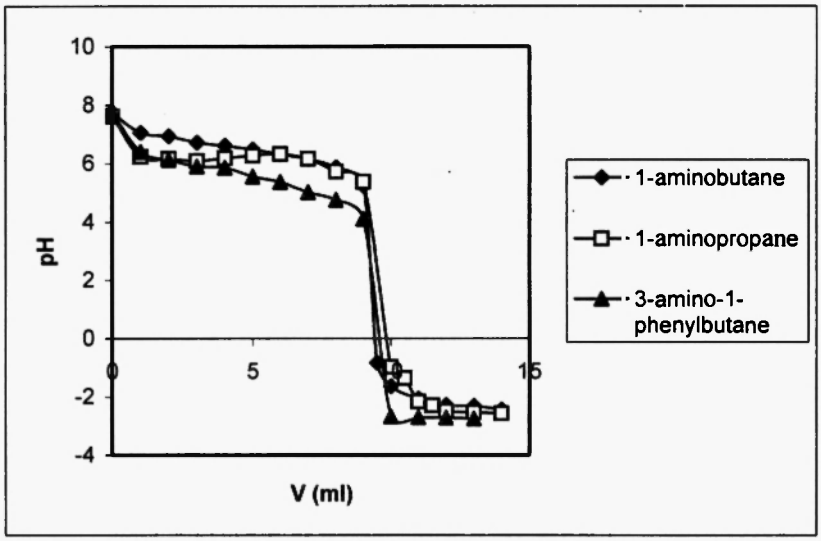

Fig. 2: Potentiometric titration curve of primary amines with HCl in toluene solvent (pH-V graphic)

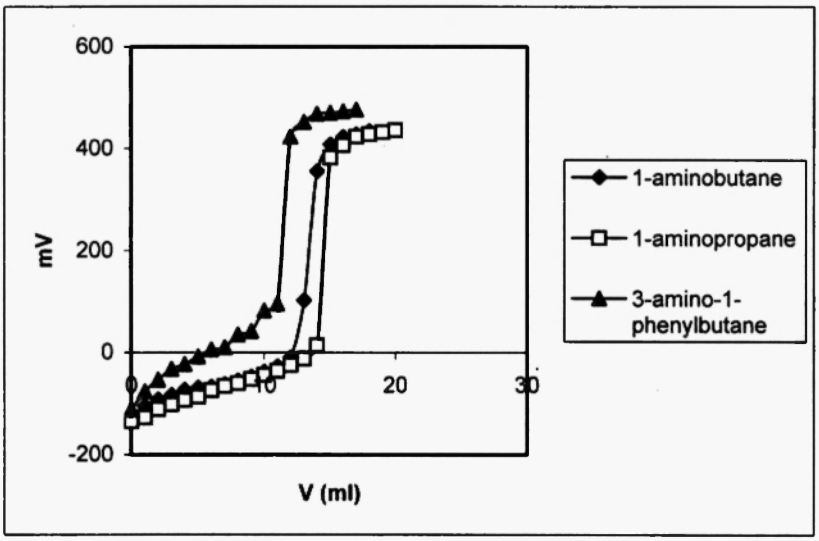

Fig. 3: Potentiometric titration curve of primary amines with HCl in methanol solvent (mV-V graphic)

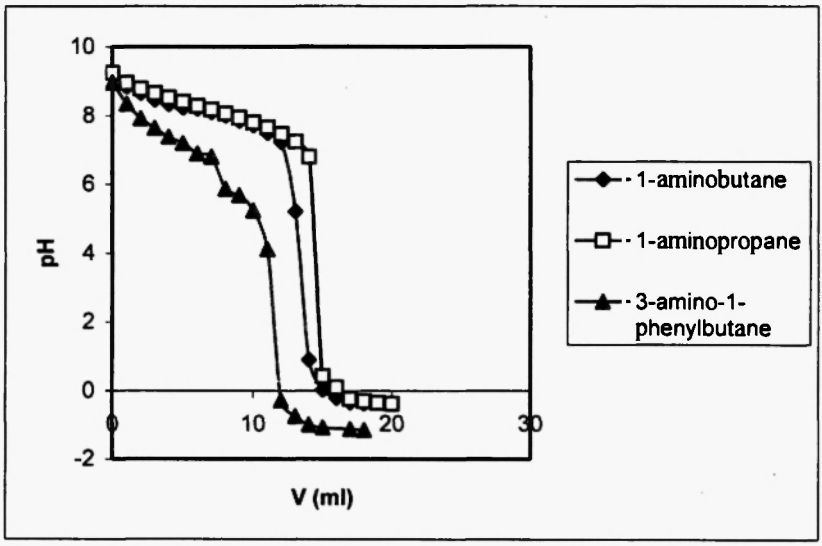

Fig. 4: Potentiometric titration curve of primary amines with HCl in methanol solvent (pH-V graphic)

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.

Titration curves, produced plotting the exchange of electrode potential difference against to titrant, of the 1-amino butane, 1-aminopropane and 3-amino-1-phenylbutane solved in toluene: MeOH (methanol) (95:5) mixture, with HCl in toluene solvent (0.1 M) are given in Figures 1-2. Titration of these weak bases with HCl in toluene gave well defined and stochiometric end-points with potential jumps ranging from 100 to 500 mV as a large potential break occurred at the equivalence points. Such potential jumps are considered to be very good for non-aqueous medium titrations. The recovery percentage of the titrated substances was calculated as 95.96 %, 102 % and 89.25 %, and the half-neutralization potentials are 277, 278 and 316 mV respectively for 1-aminobutane, 1-aminopropane and 3-amino-1-phenylbutane for toluene-HCl system. The basicity order of the studied amines in toluene is 1-aminobutane >1-aminopropane > 3-amino-1-phenylbutane.

The same weak bases were 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 Figures 3 and 4. The half- neutralization potentials are 183, 198 and 244 mV respectively for 1-aminobutane, 1-aminopropane and 3-amino-1-phenylbutane for MeOH-HCl system.

Titrations carried out with non-aqueous toluene with a very small amount of alcohol, which can be autoprotolysed, show definite and 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 methanol amount increases, a large pH change is observed at the small amounts of acid consumption.

Also, the results of pH-V graphics show that there is a decrease in pH values with increase of volume.

As a result of this study, inert and aprotic solvent toluene is suitable for the titration of weak bases in non-aqueous media as solvent, although benzene, which is a more carcinogenic aromatic hydrocarbon, is 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 amounts of amphiprotic solvents.

HCl is also a good titrant for weak bases because of its great solubility in most solvents; i.e. 0.58 N in toluene and 0.86 N in MeOH at saturation point and availability from the cheap compounds such as NaCl and H_2SO_4.

The method used for non-aqueous titrations of weak bases is also an easily applicable and convenient method in every laboratory and the non-aqueous titrations could be used widely in different applications.

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