

Non-aqueous Conductimetric Titrations of Phenolic Compounds with Tetra-*n*-butyl Ammonium Hydroxide and Amines with Perchloric Acid in Acetonitrile Solvent

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Non-aqueous conductimetric titrations were carried out for phenolic acids (2-nitrophenol, 4-nitrophenol, 3-methoxyphenol and *o*-cresol) and their mixtures dissolved in acetonitrile with tetra-*n*-butyl ammonium hydroxide dissolved in propan-2-ol. Also non-aqueous conductimetric titrations were carried out for amines (aniline and benzylamine) and their mixtures dissolved in acetonitrile with perchloric acid dissolved in dioxane. The non-aqueous conductimetric titration results have been interpreted in terms of the relative acid and basic strength of the phenolic acids and the amines. The results distinguish non-aqueous titrations from those carried out in aqueous medium

Key Words: Non-aqueous conductimetric titration, Phenolic compounds, Tetra-*n*-butyl ammonium hydroxide, Perchloric acid, Acetonitrile solvent.

INTRODUCTION

The titration of acids and bases in non-aqueous media dates back to the 1930's¹⁻⁴. The first comprehensive review of this subject did not appear until 1973 and was compiled by Fritz⁵. Conductimetric titration is one of the analytical techniques available to measure ionic concentrations and it has scope for wide applications in the industry. Phenolic acids⁶ and amines have received good attention for conductimetric titration over the last years but not many studies appeared about their mixtures. Acetonitrile^{6,7} is one of the best solvents for the titrations of phenolic acids and amines not only because it dissolves these compounds in sufficient concentrations at room temperature but also it is a dipolar aprotic and protophobic solvent. In this work, individual phenolic acids (2-nitrophenol, 4-nitrophenol, 3-methoxyphenol and *o*-cresol) and their mixtures dissolved in acetonitrile were titrated conductimetrically with tetra-*n*-butyl ammonium hydroxide dissolved in propan-2-ol. Also individual amines (aniline and benzylamine) and their mixtures dissolved in acetonitrile were titrated conductimetrically with perchloric acid dissolved in dioxane. The results have been interpreted in terms of the relative acid and basic strengths of the phenolic acids and the amines⁸.

EXPERIMENTAL

Potassium chloride (99.5%), *o*-cresol (98% pure), aniline (99.5%) and benzylamine (99.5%) were purchased from BDH. The solvents acetonitrile (98%),

dioxane and propan-2-ol (min. assay 99.85%) were also purchased from BDH. 4-Nitrophenol (98% pure) was purchased from Labosi. 3-Methoxyphenol (96% pure) and 2-nitrophenol (98% pure) were purchased from Aldrich. Tetra-*n*-butyl ammonium hydroxide solution in propan-2-ol and methanol was purchased from Merck. All the chemicals were used without further purification.

A Jenway model 4310 conductivity-meter equipped with probes of the types 027012 and 027028, having a black platinum film on the cell plated was used. Prior to conductimetric titration, the apparatus was calibrated with the conductivity cell immersed in 0.010 M potassium chloride solution. All titrations were carried out at room temperature.

Procedure

The solution to be titrated was pipetted into a beaker, it was diluted with about 50 mL of acetonitrile and the magnetic stirrer was set in motion. The titrant was then added from a burette graduated with 0.05 mL divisions. The titrant was added in small portions with the solution in the beaker under constant magnetic stirring. The conductivity of the mixture was noted once the reading on the meter got stabilized. In many cases preliminary titrations were carried out to provide information as to the increments of the titrant best suited for the particular titration. Each titration was repeated twice and the average value was calculated.

RESULTS AND DISCUSSIONS

The results of the conductimetric titrations of phenolic compounds in acetonitrile with 0.200 M tetra-*n*-butyl ammonium hydroxide in propan-2-ol are given in Table-1.

The acidic property of the phenolic compounds is due to the dissociation of the phenolic proton. The initial average conductivity of all the phenolic titrands on acetonitrile was very low before the titrations began. In all cases the conductimetric plots (Fig. 1) consist of lines, the slope of the best-fit line before the end point is greater than that of the best fit line after the end point. Thus as the titrant tetra-*n*-butyl-ammonium hydroxide was being added to the phenolic titrand, con-

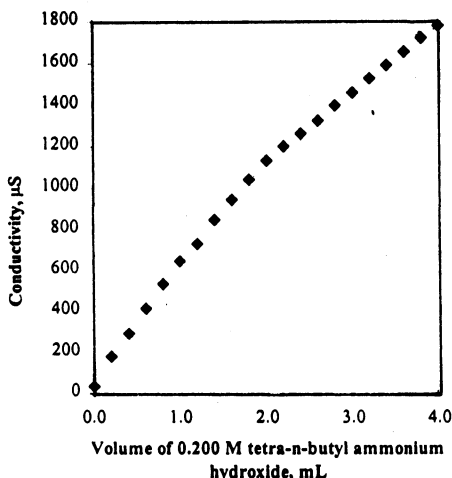


Fig. 1. Titration of 2.00 mL 4-nitrophenol (0.200 M) with tetra-*n*-butyl ammonium hydroxide (0.200 M) in acetonitrile

ductivity increased quite rapidly up to the end point and after that the conductivity still increased but less significantly. In the case of titration of binary mixtures of the phenols, a similar trend is observed and the increase in conductivity after the second end point is even less than that from the first end point up to the second end point (Fig. 2).

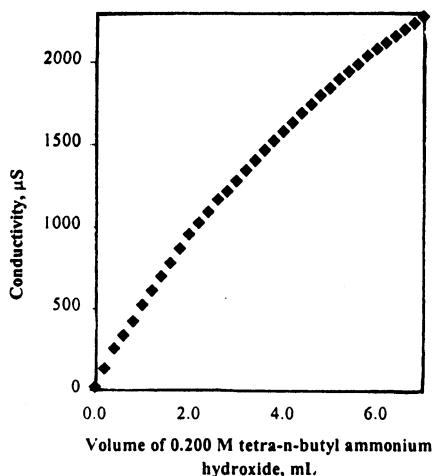


Fig. 2. Titration of 2.00 mL 4-nitrophenol (0.200 M) + 2.00 mL 3-methoxyphenol (0.200 M) with tetra-*n*-butyl ammonium hydroxide (0.200 M) in acetonitrile

TABLE-1
CONDUCTIMETRIC TITRATIONS OF PHENOLIC COMPOUNDS IN ACETONITRILE
AGAINST 0.200 M TETRA-*n*-BUTYL AMMONIUM HYDROXIDE 0.200 M

Titrand	Average volume of 0.200 M tetra- <i>n</i> -butyl ammonium hydroxide (mL)	Percentage deviation from stoichiometric end point (%)
2.00 mL of 0.200 M 4-nitrophenol	1.95	-2.5
2.00 mL of 0.200 M 3-methoxyphenol	2.05	+2.5
2.00 mL of 0.200 M 4-nitrophenol + 3.00 mL of 0.200 M 3-methoxyphenol	2.10 for 4-nitrophenol 2.75 for 3-methoxyphenol	+5.0 -8.3
2.00 mL of 0.200 M <i>o</i> -cresol	1.95	-2.5
2.00 mL of 0.200 M 4-nitrophenol + 3.00 mL of 0.200 M <i>o</i> -cresol	2.00 for 4-nitrophenol 2.85 for <i>o</i> -cresol	nil -5.0
2.00 mL of 0.200 M 2-nitrophenol	2.00	nil
2.00 mL of 0.200 M 4-nitrophenol + 3.00 mL of 2-nitrophenol	2.10 for 4-nitrophenol 2.75 for 2-nitrophenol	+5.0 -8.3

It is thought that when the active species in a solution whose conductivity is being measured, tend to exist as ion-pairs or ion aggregates in the solvent, the

conductivity is low.⁹ Also, when a charge tends to remain localized on an atom, ion-pair formation is favoured and this leads to a low conductivity. Phenolate ions do not readily undergo homoconjugation reaction $HA + A^- \longrightarrow HA_2^-$. Homoconjugates HA_2^- are better conductants than their anions, because negative charge is more delocalized over a larger anion. The monotone increase in conductivity after the end point is due to the charge delocalization brought about by resonance in the phenolates. As the resonance form stabilizers, the phenolates, they do not form homoconjugates. The stronger the resonance system in an anion, the more stable it is and hence the less likely for it to undergo homoconjugation⁷. From the beginning of the titration up to the end point tetra-*n*-butyl ammonium cation and phenolate anion are present in the titrand. However, the tetra-*n*-butyl ammonium cation has little tendency to form ion pairs, thus conductivity of the titrand increased steadily¹⁰. After the end point, the titrand solution gets enriched with hydroxide ion. Unlike in aqueous medium, the mobility of hydroxide ion in a dipolar aprotic solvent like acetonitrile is very restricted^{6, 11}. Hence, conductivity does not increase so sharply as in aqueous medium with increasing hydroxide ion concentration. Two factors play important roles in the shape of titration curves¹². These are: (i) intra- and intermolecular hydrogen bonding and (ii) formation of ion-pairs. Hydrogen bonding tends to lower the conductivity by making the molecules or ions less mobile in the solvent. In the case of binary mixtures, the first end point, like in aqueous titrations, corresponds to the stronger acid and the second end point to the weaker acid in the mixture. The phenols present in the binary mixtures were not in equimolar amounts and this has helped in deciding which phenol reacted first or second during addition of titrant tetra-*n*-butyl ammonium hydroxide. The results obtained in this are in agreement with what theory says concerning the relative strength of the phenols.

The results of the conductimetric titrations of amines in acetonitrile with 0.200 M perchloric acid in dioxane are given in Table-2.

TABLE-2
CONDUCTIMETRIC TITRATIONS OF AMINES IN ACETONITRILE AGAINST
0.200 M PERCHLORIC ACID IN DIOXANE

Titrand	Average volume of 0.200 M perchloric acid (mL)	Percentage deviation from stoichiometric end point (%)
2.00 mL of 0.200 M aniline	1.95	-2.5
2.00 mL of 0.200 M benzylamine	1.95	-2.5
2.00 mL of 0.200 M benzylamine + 3.00 mL of 0.200 M aniline	2.10 for benzylamine 2.65 for aniline	+5.0 -11.7

These titrations were done in the presence of an excess of acetonitrile. These two differ in their basic strength and this is confirmed in the conductimetric plot for the titration of the mixture (benzylamine + aniline) against perchloric acid. The amines were not present in equimolar amounts in the initial binary mixture

in order to facilitate recognition of the end point for each amine. The first end point corresponds to the neutralization of the stronger base benzylamine while the second end point is that for aniline. This is in agreement with the molar quantities of the two bases. Here also, the titration results are more stoichiometric when the amine is present alone instead of being part of a mixture of amines. The titre values obtained when each amine was present alone in the titrand differ by only 0.05 mL from what stoichiometric relationships predict.

The conductimetric titration curves of the amines resemble those of the phenols studied in the sense that the slope of the best-fit line before the end point is greater than that of the best-fit line after the end point (Fig. 3). Thus as titrant perchloric

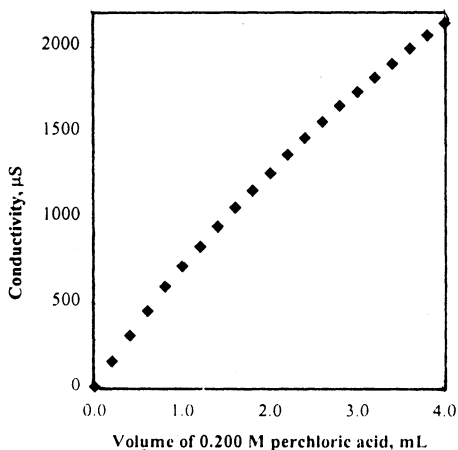


Fig. 3. Titration of 2.00 mL benzylamine (0.200 M) with perchloric acid (0.200 M) in acetonitrile

acid was being added to the amine titrand, conductivity increased quite rapidly up to the end point and after that the conductivity still increased with added titrant but less significantly. In the case of titration of binary mixtures of the amines, the same situation arises and the increase in conductivity after the second end point is even less than that from the first end point up to the second end point. The initial average conductivity of the amine titrand in acetonitrile was very low before the titrations began, for example, the conductivity of aniline and benzylamine were 7.24 and 7.15 μS respectively. After the end point, all the aniline initially present in the titrand had turned into aminium cation. As addition of perchloric acid titrant was continued, the solution was getting enriched with perchlorate anion. The latter can use the lone pairs of electrons on its anionic oxygen to form hydrogen bond with the aminium cation. Thus, beyond the end point, the amount of hydrogen bonding in the titrand was increasing. Consequently this reduced the mobility of the ions and hence conductivity increased less significantly than before the end point was reached. After the end point, the titrand solution gets enriched with hydrogen ion. Unlike in aqueous medium, the mobility of hydrogen ion in a dipolar aprotic solvent like acetonitrile is very restricted¹. Hence,

conductivity does not increase so sharply as in aqueous medium with increasing hydrogen ion concentration

Conclusion

Thus this paper illustrates some of the aspects of non-aqueous conductimetric titrations exemplified by the titrations of phenolic acids and their mixtures dissolved in acetonitrile with tetra-*n*-butyl ammonium hydroxide dissolved in propan-2-ol. Conductimetric tirations have also been done for amines (aniline and benzylamine) and their mixtures dissolved in acetonitrile with perchloric acid dissolved in dioxane. The results have been analysed in terms of relative strength of acid and bases. It is found that the results agree with various concepts available in the literature. Also the results obtained distinguish non-aqueous titrations from those carried out in aqueous medium.

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