Conductometric Estimation of Strong Acid Mixtures using Barium Acetate

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The present paper describes conductomeric estimations of strong acid mixtures taking binary systems using barium acetate in presence of large excess of some non-aqueous solvents. The binary systems involved are: (a) $H_2SO_4 + HCl$, (b) $H_2SO_4 + HNO_3$ and the non-aqueous solvents used were acetone and glacial acetic acid. Estimations of H_2SO_4 in these systems have been found to be most satisfactory. However, estimations of HCl and HNO_3 in these systems show some deviations when results are compared with single titrations. A suitable titrant such as lead acetate has also been proposed for the estimation of these binary systems of strong acids.

INTRODUCTION

Samples present in non-aqueous solvent can be conductometrically titrated using reagents such as alcoholic sodium hydroxide, perchloric acid etc. as titrants. A large number of weak organic acids in methanol, dimethyl formamide and pyridine can be titrated using tetramethyl ammonium hydroxide and potassium methoxide in methanol-benzene and pyridine-benzene. The mixtures of weak bases with perchloric acid in dioxane-formic acid solvent system have also been conductometrically estimated. Mixtures of strong acids like H₂SO₄ plus HCl, in anhydrous acetic acid, using lithium acetate in the same solvent as titrant, have also been titrated and reported in the literature¹⁻⁷. In this way non-aqueous acid-base titrations have been extensively studied, but the work on conductometric estimation of strong acid mixtures using appropriate reagents in presence of large excess of non-aqueous medium is still scanty.

The present study decribes a new analytical method providing conductometric estimation of strong acid mixtures using barium acetate in presence of large excess of non-aqueous medium. Non-aqueous mediums included are acetone and glacial acetic acid for conductometric estimation of strong acid mixture systems involving (a) H₂SO₄ plus HCl, (b) H₂SO₄ plus HNO₃.

EXPERIMENTAL

B.D.H or A.R. brand chemicals were used in the present study. The conductance measurements were carried out by using the modern conductivity bridge (systronic make). De-ionised low conductivity water has been used in the preparation of

solution in aqueous medium. This is in accordance with the fact that the conductivity water is not essential for carrying out conductometric titrations.

Following conductometric titrations have been performed:

- (i) Titration of H_2SO_4 vs $Ba(OAc)_2$: 5 Ml of approximately 0.5 N H_2SO_4 was taken in the conductivity cell and 95 ml of de-ionised low conductivity water was added to it. From burette 0.5 N $Ba(OAc)_2$ solution prepared in de-ionised low conductivity water was added slowly. For each volume of $Ba(OAc)_2$ added, the conductance of the resulting mixture was measured. A graph between conductance values and the volumes of $Ba(OAc)_2$ added gives clearly an end point of the titration.
- (ii) Titration of HCl vs Ba(OAc)₂ and HNO₃ vs Ba(OAc)₂: The same procedure as given in (i) has been followed to perform these titrations also. 5 Ml of approximately 0.5 N HCl or 5 ml of approximately 0.5 N HNO₃ instead of 0.5 N H₂SO₄ has been used in the titrations.
- (iii) Titrations of H₂SO₄ plus HCl vs Ba(OAc)₂ in presence of acetone as well as in glacial acid taken in large excess: 5 ml of H₂SO₄ of same strength as used in single titration (i) and 5 ml. of HCl of same strength as used in single titration (ii) were taken in the conductivity cell. To this mixture 40 ml of acetone or acetic acid (glacial) has been added. From the burette 0.5 N Ba(OAc)₂ was slowly added. In the beginning conductance value remains constant upto a certain limit and then it decreases in a certain order upto some extent. The order of decrease in conductance value is changed thereafter when addition of Ba(OAc)₂ solution was continued slowly. After certain readings the values of conductance go on increasing. When conductance values are plotted against volume of Ba(OAc)₂ added then two end points are clearly obtained. From the end points the estimation of each strong acid in the mixture can be computed.

RESULTS AND DISCUSSIONS

Conductometric titrations involving single strong acid and Ba(OAc)₂ have been reported in Table 1. Conductometric titrations of H₂SO₄ plus HCl mixture with Ba(OAc)₂ in the presence of large excess of acetone and glacial acetic acid have been reported in Table 2. Conductometric titrations of H₂SO₄ plus HNO₃ mixture with Ba(OAc)₂ in presence of large excess of acetone and glacial acetic acid have been reported in Table 3.

The results of the above conductometric titrations can be summarised as follows:

(i) Conductometric estimation of H_2SO_4 in the mixture of $H_2SO_4 + HCl$ or $H_2SO_4 + HNO_3$ using $Ba(OAc)_2$ has been found suitable in both acetone and glacial acetic acid taken in large excess. However % error in the estimation of H_2SO_4 in mixture of $H_2SO_4 + HNO_3$ in presence of large excess of glacial acetic acid is much deviated in the said titrations.

TABLE 1
CONDUCTOMETRIC TITRATIONS INVOLVING SINGLE
STRONG ACID AND Ba(OAc)₂

Strong acid	Vol. of 0.5 N Ba(OAc) ₂ used	Concentration of strong acid	
5 ml of H ₂ SO ₄	7 ml	0.70 N	
+ 95 ml. of water			
5 ml of HCl	4.4 ml	0.44 N	
+ 95 ml. of water			
5 ml. of HNO ₃	3.6 ml	0.36 N	
+ 95 ml. of water			

TABLE 2
CONDUCTOMETRIC TITRATIONS OF H₂SO₄ + HCI
MIXTURE WITH Ba(OAc)₂ IN PRESENCE OF LARGE EXCESS
OF ACETONE AND GLACIAL ACETIC ACID

Strong acid mixture	Vol. of 0.5 N Ba(OAc) ₂ used		Concentration of acid	
	for H ₂ SO ₄	for HC1	H ₂ SO ₄	HC1
5 ml of H ₂ SO ₄ + 5 ml of HCl + 40 ml of acetone	7 ml	4.9 ml	0.70 N	0.49 N
5 ml of $H_2SO_4 + 5$ ml of $HCl + 40$ ml of glacial acetic acid	7 ml	4.5 ml	0.70 N	0.45 N

TABLE 3
CONDUCTOMETRIC TITRATIONS OF H₂SO₄ + HNO₃ MIXTURE WITH Ba(OAc)₂ IN PRESENCE OF LARGE EXCESS OF ACETONE AND GLACIAL ACETIC ACID

Strong acid mixture	Vol. of 0.5 N Ba(OAc) ₂ used		Concentration of Acid	
	for H ₂ SO ₄	for HNO ₃	H ₂ SO ₄	HNO ₃
5 ml. of $H_2SO_4 + 5$ ml. of $HNO_3 + 40$ ml. of acetone	7 ml	3.0 ml	0.70 N	0.30N
5 ml. of H ₂ SO ₄ + 5 ml. of HNO ₃ + 40 ml. of glacial acetic acid	6.3 ml	4.6 ml	0.63 N	0.46 N

⁽ii) Conductometric estimation of HCl in the mixture of $H_2SO_4 + HCl$ using $Ba(OAc)_2$ in both acetone and glacial acetic acid taken in large excess has been found to be satisfactory. The % error is found to be less when the conductometric titration is carried out in presence of glacial acetic acid medium (2.3%) in comparison to acetone medium (11.1%).

(iii) Conductometric estimation of HNO₃ in the mixture of H₂SO₄ + HNO₃

using $Ba(OAc)_2$ has been found to be less satisfactory when it is carried out in acetone medium (% error comes to be 16.6%). However, if this titration is carried out in glacial acetic acid medium taken in large excess then % error comes to be 27% which shows much deviation. Hence some other suitable non-aqueous medium is to be preferred.

- (iv) In these titrations the conductance values of the resulting mixture in conductivity cell have been found to be in agreement with the replacement reactions involved as follows:
 - (a) At the stage of first end point,

$$H^+ + \frac{1}{2}SO_4^- + H^+ + Cl^- + (\frac{1}{2}Ba^{++} + OAc^-) \rightarrow \frac{1}{2}BaSO_4 \downarrow + AcOH + H^+ + Cl^-$$

In conductivity cell From burette

(b) At the stage of second end point

$$H^+ + Cl^- + (\frac{1}{2}Ba^{++} + OAc^-) \rightarrow \frac{1}{2}Ba^{++} + Cl^- + AcOH$$

In conductivity cell From burette

The present study can however be extended while using other suitable titrants such as lead acetate in presence of some common non-aqueous solvents.

CONCLUSIONS

The conductometric estimations of strong acid mixtures taking binary systems have been successfully carried out in some suitable non-aqueous solvents taken in large excess. This provides a newer analytical method for conductometric estimation of strong acid mixture.

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