Thermodynamic and Kinetic Implications Involved in the Titration of Polyfunctional Acids by Catalytic Thermometric Titrimetry

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The influence of the concentration of reactants on the results of titrations of salicylic acid in acetone with potassium and tetramethylammonium hydroxides in propan-2-ol were investigated. The titrations were performed by catalytic thermometric titrimetry using acetone as the end-point indicator and by potentiometric titrimetry. These and other results are discussed in terms of the equilibrium and kinetic aspects involved in the titrations of polyfunctional acids capable of forming intramolecular hydrogen bonds.

Keywords: *Catalytic titrimetry, thermometric titrimetry, hydrogen bond, salicylic acid*

Vaughan and Swithenbank[1] introduced acetone as a thermometric end-point indicator in the titration of a variety of acidic substances with strong bases. In their method, the rise in temperature, caused by the exothermic reaction of dimerization of acetone catalysed by the excess of strong bases, is employed to locate the end-point of the titration.

Greenhow and co-workers[2–6] performed an extensive and systematic study of the titration of polyfunctional acids by catalytic thermometric titrimetry. They have shown the possibility of obtaining selectivity by appropriate control of the stoichiometry at the end-point of the titration. According to these workers, the variation of stoichiometry can be attained by choosing the appropriate end-point indicator, sample solvent, titrant or in some instances the concentration of titrant.

They have investigated more specifically the influence of titrant and sample solvent on the stoichiometry attained in the titration of some hydrogen bonded polyfunctional acids.[5] The influence of the sample solvent is related to the extent of dissociation of the titrant ion-pair with potassium hydroxide as titrant whereas tetrabutylammonium hydroxide is considered to be completely dissociated. A mechanism, which considered the formation of a four-centre intermediary between the half-neutralized difunctional acid and the potassium hydroxide ion-pair, was presented to explain the results. The neutralization and indicative reactions are considered to be competitive processes.

In this paper, a study of the influence of the sample and titrant concentrations on the titration of salicylic acid (in acetone) with potassium hydroxide (in propan-2-ol) is presented. The results are compared with those obtained by using tetramethylammonium hydroxide as the titrant.

These and other results, in the literature, are explained by considering the thermodynamic and kinetic aspects involved in the titrations of polyfunctional acids capable of forming intramolecular hydrogen bonds. In this context, the influence of the nature of the titrant and concentrations of both titrant and sample on the extension and rate of neutralization reactions are discussed. The mechanism employed to relate the rate of neutralization reaction of polyfunctional acids, capable of forming intramolecular hydrogen bonds, with the concentration of sample and titrant is based on recent investigations by Hibbert and Spiers.[7] These workers investigated the kinetics of the removal of protons from substituted salicylates, by hydroxyl ions and buffers. Finally, the comparison of the rates of neutralization and catalysed reactions is employed to discuss the stoichiometries obtained at the end-point.

Experimental

Reagents

Salicylic acid and potassium hydroxide were of analytical-reagent grade. Acetone and propan-2-ol, of laboratory-reagent grade, were dried with 3 Å molecular sieves before use.

Solutions of 0.5 and 1.0 mol dm^{-3} potassium and tetramethylammonium hydroxide in propan-2-ol were prepared and standardized with benzoic acid in ethanol using phenolphthalein as indicator. Other solutions were prepared by appropriate dilution of the 0.5 and 1.0 mol dm^{-3} solutions in propan-2-ol.

Apparatus

A motor driven micrometer syringe, as described by Greenhow and Spencer,[8] was employed to introduce the titrant at a constant delivery rate in both the potentiometric and thermometric titrations. In the thermometric titrations the temperature changes were detected by means of a thermistor placed in one arm of a Wheatstone bridge, and were recorded on a strip-chart recorder as described elsewhere.[9] A Micronal B 375 pH meter, a platinum electrode and a nichrome wire inserted into the titrant solution were employed in the potentiometric titrations.

Procedure

In the thermometric titrations, the desired volume of salicylic acid solution was pipetted into a 25 ml unsilvered Dewar flask and diluted with acetone to 10 ml. In both the potentiometric and thermometric titrations the titrant was added at a constant delivery rate of 0.13 ml min^{-1}. During the titrations the solutions were stirred with a magnetic stirrer. The amount of salicylic acid was adjusted in order that the volume of titrant delivered at the end-point of titration was between 0.25 and 0.5 ml. The concentration of propan-2-ol was kept between 2.5 and 5.0%.

Results and Discussion

The results of the titrations of salicylic acid in acetone with potassium and tetramethylammonium hydroxides in propan-2-ol by catalytic thermometric titrimetry are presented in Fig. 1. For potassium hydroxide, it was observed that the stoichiometry attained at the end-point increases from ≈1 to

≈2 when the concentration of the titrant is increased from 0.01 to 0.5 mol dm^{-3}. It was also observed that when the titrant is tetramethylammonium hydroxide, only one group is titrated and the stoichiometry is independent of the concentration of the reactants.

The results obtained by thermometric titrimetry with tetramethylammonium hydroxide as titrant are explained by considering the small second dissociation constant of salicylic acid. Consequently, the concentration of hydroxyl ions necessary to start the catalysed reaction is attained before the second equivalence point. In fact, as can be seen in Fig. 2, the dissociation constant is not sufficiently large to produce the second inflection in the potentiometric titration curve of salicylic acid with 0.1 and 0.8 mol dm^{-3} tetramethylammonium hydroxide solutions. However, the inflection corresponding to the titration of the phenolic group (absent when 0.1 mol dm^{-3} potassium hydroxide is used) is observed when 1.0 mol dm^{-3} potassium hydroxide is used as the titrant.

Another point to be considered is that when potassium hydroxide is used as the titrant at concentrations above 0.1 mol dm^{-3}, the formation of a white precipitate of potassium salicylate is observed. Therefore it is necessary to consider, in addition to the neutralization reaction, the precipitation of potassium salicylate.

$$HSal^- + OH^- \rightleftharpoons Sal^{2-} + H_2O \quad (1)$$

$$Sal^{2-} + 2K^+ \rightleftharpoons K_2Sal(s) \quad (2)$$

The precipitation of potassium salicylate causes a displacement to the right of the equilibrium represented in eqn. (1).

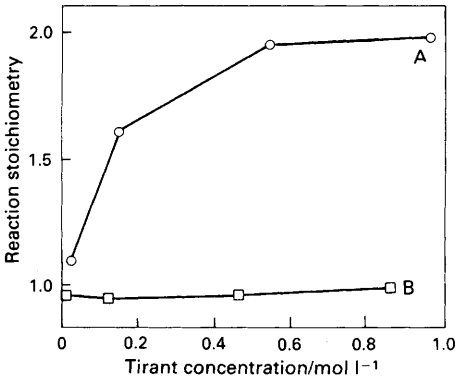
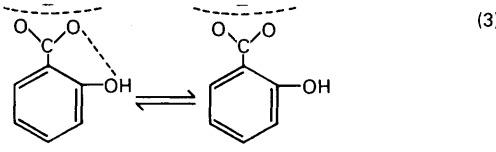


Fig. 1 Effect of concentration on the titration of salicylic acid in acetone by catalytic thermometric titrimetry. Titrant: A, KOH in propan-2-ol; and B, Me_4NOH in propan-2-ol. Volume of acetone, 10 ml. Concentration of salicylic acid = 1/40 of the concentration of the titrant

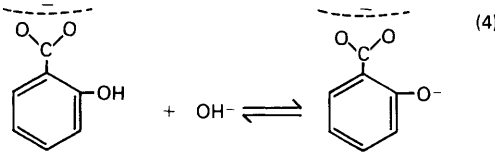
Therefore, if potassium hydroxide is used in place of tetramethylammonium hydroxide, the reaction in eqn. (1) will occur, to a large extent, before the concentration of hydroxyl ions reaches the value necessary to start the catalysed reaction.

Furthermore, in catalytic titrimetry it is necessary to consider the competition between the determinative and the indicative reactions.[5,6] These implications are particularly important in the titration of hydrogen bonded acids, as with the second acidic group of salicylic acid, where the rates of the neutralization reaction are not diffusion controlled as for normal acids.[10]

According to Hibbert and Spiers,[7] the removal of the second proton from substituted salicylates involves two steps; breaking of the hydrogen bond and proton transfer. For salicylic acid, these two steps are represented by the following equations:



(3)



(4)

These workers have shown in their studies using dimethyl sulphoxide–water mixtures that, for concentrations of hydroxyl ions above 0.02 mol dm^{-3}, the breaking of the hydrogen bond is the rate-limiting step and that below this value the proton transfer is the rate-limiting step. In the range of concentration of hydroxyl ions below 0.02 mol dm^{-3}, the rate of the reaction increases linearly with the increase of concentration of hydroxyl ions. Above this value the rate of reaction varies little and tends to be independent of the concentration of hydroxyl ions.

In the application of this mechanism to these results, it is assumed that when using potassium hydroxide as the titrant the concentration of hydroxyl ions is in the concentration range where proton transfer is the rate-limiting step. This assumption is reasonable as, in this medium, potassium hydroxide is present mainly as ion pairs.[5,6] Consequently, the rate of the neutralization reaction increases to a larger extent than that of the catalysed reaction with the increase of

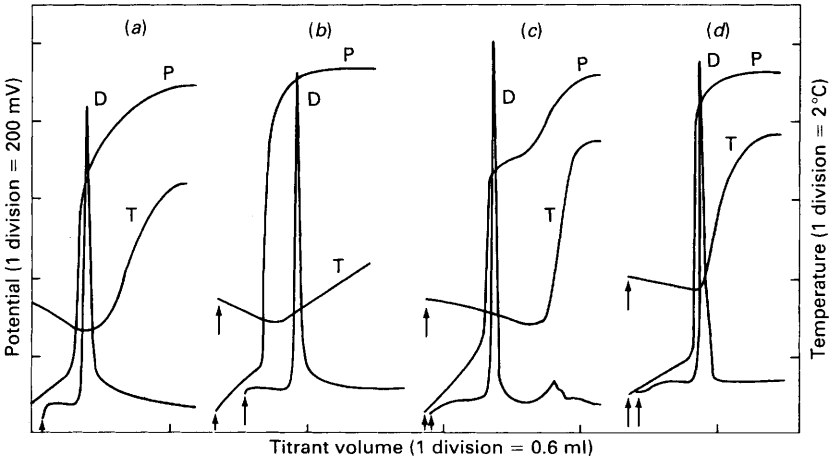


Fig. 2 Potentiometric and thermometric titration curves of salicylic acid in acetone. Concentration of salicylic acid = 1/40 of the concentration of the titrant. Volume of acetone, 10 ml. (*a*) KOH 0.1 mol dm^{-3} in propan-2-ol; (*b*) Me_4NOH 0.1 mol dm^{-3} in propan-2-ol; (*c*) KOH 1.0 mol dm^{-3} in propan-2-ol; and (*d*) Me_4NOH 0.8 mol dm^{-3} in propan-2-ol. P, Potentiometric titration curve; D, first derivative of potentiometric titration curve; and T, thermometric titration curve. The arrows indicate the start of the titrations

concentration of potassium hydroxide. This mechanism is consistent with the fact that the stoichiometry at the end-point increases with an increase in the concentration of potassium hydroxide and salicylic acid. The fact that the phenolic group of salicylic acid is not titrated at the end-point with tetramethylammonium hydroxide has already been explained by considering the value of the dissociation constant of the acid.

However, Greenhow and Shafi[5] have compared the titration of a variety of polyfunctional acids with tetrabutylammonium and potassium hydroxide by employing acrylonitrile as the end-point indicator. Among the acids investigated, the benzenecarboxylic acids are of particular interest to the kinetic considerations studied in this paper. They have shown that, while all of the acidic groups are titrated with 0.5 mol dm^{-3} potassium hydroxide as the titrant, only some of these groups are titrated with 0.1 mol dm^{-3} tetrabutylammonium hydroxide. This behaviour is observed in benzenecarboxylic acids, with the exception of terephthalic acid, capable of forming intramolecular hydrogen bonds. These differences in stoichiometry obtained with the two different titrants are not observed when using benzenecarboxylic acids, which do not form intramolecular hydrogen bonds.

It is not possible to explain the low stoichiometry obtained with tetrabutylammonium hydroxide on the basis of equilibrium considerations. In fact, the pK_a values for these acids in water vary from 1.40 to 6.96. As tetrabutylammonium hydroxide is completely dissociated,[5,6] it is supposed that the concentration of hydroxyl ions is in the concentration range where the breaking of the hydrogen bond is the rate-limiting step. Therefore, when the rate of production of the 'opened' form of the acid [eqn. (3)], capable of reacting with hydroxyl ions, is not sufficiently high, an excess of hydroxyl ions sufficient to start the catalysed reaction is available. When potassium hydroxide is used as the titrant, ion pairs are mainly present and the concentration of hydroxyl ions is low. Therefore, it is reasonable to suppose that the system is in the concentration range where proton transfer is the rate-limiting step. Consequently, the rate of consumption of hydroxyl ions is sufficient to prevent the start of the catalysed reaction.

Finally, in order to acertain if a given acidic group of a polyfunctional acid capable of forming hydrogen bonds can be titrated at the end-point, it is necessary to consider both the thermodynamic and the kinetic implications involved in the titration. Firstly, it is necessary to consider the value of the dissociation constant of the acidic groups and also the possibility of displacement of the equilibrium by virtue of the precipitation of the anion formed. Next it is necessary to take into account that the removal of protons from such acidic groups by hydroxyl ions is not diffusion controlled as for normal acids. Either the breaking of the hydrogen bond or proton transfer is the rate-limiting step, depending on the conditions under which the titration is performed. By the appropriate choice of the conditions and by considering the competition between the neutralization and catalysed reactions, it is possible to obtain selectivity in the titrations.

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