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# Formalin and Paraformaldehyde as End-point Indicators in Catalytic Thermometric Titrimetry

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The use of formalin solution as an end-point indicator in the titration of both acids and bases in aqueous solutions was investigated. In both instances, a lowering in temperature at the end-point, due to depolymerization of poly(oxyethylene glycols), was observed. Endothermic end-points were also obtained by using paraformaldehyde as an end-point indicator in titrations of acids in aqueous solutions. The use of paraformaldehyde in the titration of very weak acids and of some sparingly soluble acids solubilized in micellar suspensions of cationic detergents was also investigated.

**Keywords:** *Catalytic thermometric titrimetry; formaldehyde; formalin; paraformaldehyde; cationic detergent*

Formaldehyde in alcoholic solutions<sup>1</sup> and acetaldehyde in aqueous and non-aqueous solutions<sup>2</sup> have already been used as end-point indicators for the determination of acids with bases by thermometric titrimetry. A method involving a combination of turbidimetric and catalytic thermometric titrimetry (CTT), using acetaldehyde as end-point indicator, for the determination of metal salts in the presence of mineral acids, has also been described.<sup>3</sup> 1,3,5-Trioxan, a cyclic polymer of formaldehyde, was used by Greenhow and Kashanipour<sup>4</sup> to indicate the end-point for titrations of organic bases in acetic acid. In these examples, the rise in temperature is used to locate the end-point of the titration.

The use of formalin in aqueous solutions as an end-point indicator for the titration of both acids and bases is described in this paper as is the behaviour of paraformaldehyde, a water-insoluble polymer of formaldehyde, as an end-point indicator in the titration of acids. Contrary to what occurs with the titration of acids using formaldehyde as end-point indicator in alcoholic solutions,<sup>1</sup> in all three examples studied in this work with aqueous solutions, endothermic end-points were observed. The reasons for the difference in behaviour of formalin in alcoholic and in aqueous solutions can be explained by considering the kinetics of the reactions of the components of formalin solutions in the presence of hydroxyl ions in the two different media. The results for the determination of acids and bases in aqueous solutions through the use of formalin, and of soluble and sparingly soluble acids by using paraformaldehyde, as an end-point indicator, are also discussed.

## Experimental

### Reagents

Hydrochloric acid, benzoic acid, phosphoric acid, sodium hydroxide, sodium carbonate and potassium hydrogenphthalate were of analytical-reagent grade. Hydrochloric acid and sodium hydroxide solutions (1.0 mol l<sup>-1</sup>) were prepared and standardized with sodium carbonate and potassium hydrogenphthalate by conventional procedures. Other acids and bases used in the titrations were of laboratory-reagent grade.

Laboratory-reagent grade methanol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol and 2-methylpropan-2-ol were used without further purification.

The cetrimide used consisted chiefly of tetradecyltrimethylammonium bromide, but also contained small amounts of C<sub>12</sub> and C<sub>16</sub> homologues.

The formalin solutions used were 37% formaldehyde, stabilized with 7 and 10% of methanol, from Merck (Darmstadt, Germany), ART 21569 and 4003, respectively.

### Apparatus

A motor-driven micrometer syringe, as described by Greenhow and Spencer,<sup>5</sup> was used to introduce the titrant at a constant delivery rate. In the thermometric titration, 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, as described elsewhere.<sup>6</sup> The titrations were performed in a 25 ml unsilvered Dewar flask, and the solutions were stirred with a magnetic stirrer during the titrations.

### Procedure

#### Use of formalin

After the desired amount of acid or base had been dissolved in 5 ml of water in a 25 ml unsilvered Dewar flask, 5 ml of formalin solution was added. The titrant (1.0 mol l<sup>-1</sup> NaOH in the determination of acids or 1.0 mol l<sup>-1</sup> HCl in the determination of bases) was added at a delivery rate of 0.13 ml min<sup>-1</sup>. It was essential that the titrations were performed as soon as the formalin solutions had been added. In the titration of some fairly strong bases, e.g., sodium carbonate, a modified procedure was used. In this instance, after the desired amount of sodium carbonate was dissolved in 4 ml of water, the solution was treated with 1 ml of 1 mol l<sup>-1</sup> acetic acid and then with 5 ml of formalin. The titration was then performed as described above.

#### Use of paraformaldehyde

After the desired amount of acid had been dissolved in 10 ml of water, 0.54–0.56 g of paraformaldehyde was added, then the titrant (1.0 mol l<sup>-1</sup> NaOH) was added at a delivery rate of 0.13 ml min<sup>-1</sup>. For sparingly soluble acids, the desired amount of acid was stirred with 10 ml of 0.04–0.06 mol l<sup>-1</sup> cetrimide until dissolution of the acid occurred; 0.54–0.56 g of paraformaldehyde was then added and the titration was performed as described for soluble acids. With paraformaldehyde, the waiting time before the start of titration had no effect on the shape of the titration curve.

The end-point was taken as the point where a tangent drawn to the main temperature-lowering curve intersects the titration curve at its higher value. The volumes of titrant used in the titration of blank solutions were subtracted from those corresponding to the titration of the different samples.

## Results and Discussion

### Formalin as End-point Indicator

Formaldehyde in aqueous solutions is known to be in equilibrium with methanediol and polymers of low relative molecular mass, with the general formula  $\text{HOCH}_2(\text{CH}_2\text{O})_n\text{CH}_2\text{OH}$ , called poly(oxymethylene glycols). In formalin solutions (37% formaldehyde and 7–10% methanol), the function of methanol is to stabilize the methanediol and the polymers through the formation of hemiacetals.<sup>7</sup>

In this work it was observed that when a solution of formalin, diluted 1 + 1 with water, is titrated with an aqueous solution of sodium hydroxide, an abrupt decrease in temperature is observed. This observation was surprising since, when an alcoholic solution of formalin is titrated with an alcoholic solution of potassium hydroxide, a rise in temperature is observed at the titration end-point.<sup>1</sup> One of the objectives of this work was to attempt to explain the reason for the difference in behaviour of formalin in alcoholic and aqueous solutions.

The thermometric titration curves obtained by the titration of formalin solution, diluted 1 + 1 with water and in the absence of acid, with  $1 \text{ mol l}^{-1}$  NaOH, are shown in Fig. 1. It is assumed that the lowering in temperature at the end-point is due to the depolymerization reaction of poly(oxymethylene glycols) catalysed by hydroxyl ions. Fig. 1 also shows that the temperature lowering at the end-point decreases with the increase in the time interval in which the diluted formalin solution is allowed to stand before the addition of titrant. These facts are explained by considering that the dilution of formalin solution also results in the dilution of methanol originally present in the solution, which stabilizes the polymers through the formation of hemiacetals.<sup>7</sup> Hence, the dilution of methanol results in a slow depolymerization of poly(oxymethylene glycols) before the titration is performed. As can be seen in Fig. 1, this reaction must be complete after about 3 h.

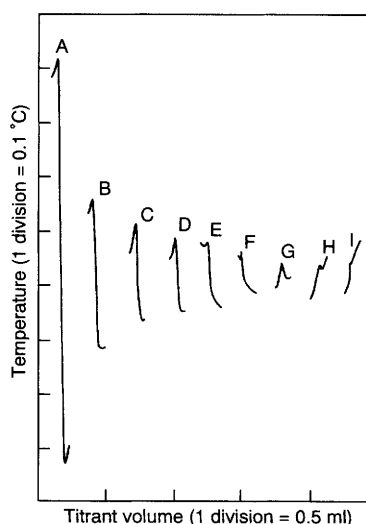
Fig. 2 shows the results of the titration of 10 ml of a solution of formalin, diluted 1 + 1, as a function of the final content of methanol. It can be seen that for solutions where the methanol content is above 10% m/m an exothermic end-point is observed and that the temperature rise at the end-point increases with the methanol concentration. However, when the methanol content is lower than 7% m/m an endothermic end-point is observed. These facts are explained by taking into

account the competition between two reactions when the diluted formalin solution is treated with sodium hydroxide, the depolymerization of poly(oxymethylene glycols), which is endothermic, and the Cannizzaro reaction, which is an exothermic reaction. Consequently, the depolymerization reaction predominates when the methanol content is low, and the Cannizzaro reaction predominates when the methanol content is high. In some instances, it is possible to observe an exothermic effect followed by an endothermic effect or *vice versa*. The hypothesis that the formation of hemiacetals leads to the predominance of Cannizzaro reaction is also supported by the results shown in Fig. 3. From these it can be seen that the formation of hemiacetals increases in the order: primary > secondary > tertiary alcohols.

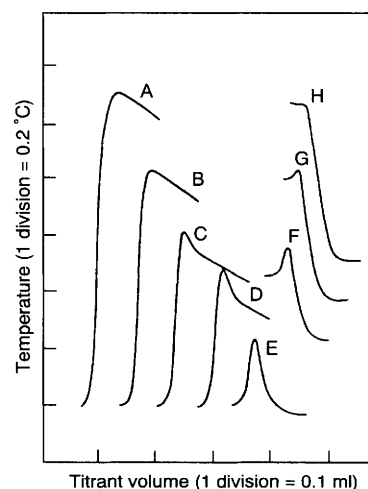
Some thermometric titration curves for acids, with formalin as the end-point indicator, are shown in Fig. 4, and results are presented in Table 1. In the example of phosphoric and of succinic acids, 2 mol of  $\text{H}^+$  per mol of acid are titrated. One problem in these titrations is the poor reproducibility of the thermometric titration curves.

Similar to what happens for bases, the depolymerization of poly(oxymethylene glycol) present in formalin solution is also catalysed by acids. As can be seen in Fig. 5, where the thermometric titration curves for the titration of some bases with strong acid are shown, a lowering in temperature is observed at the end-point. The endothermic effect observed when formalin solutions are treated with strong acid is in agreement with the studies of Wadano *et al.*<sup>8</sup> According to these authors, the rate of depolymerization of formaldehyde in solution is slow in the pH range 2.6–4.3, but increases very quickly at higher and lower pH values. It was observed in this work that, by using a formalin solution (37% in formaldehyde and 7–10% in methanol), diluted 1 + 1 with water, an abrupt lowering in temperature occurred at pH 2.1 and 9.0.

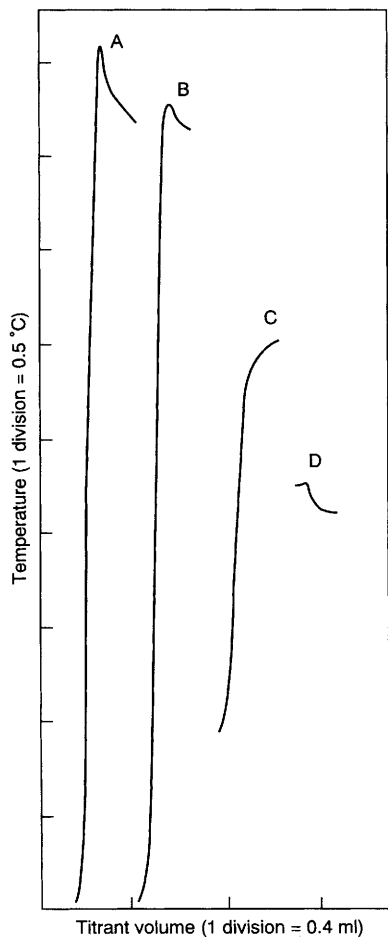
As can be seen in Table 1, the method can be applied to weak bases such as acetate ( $\text{p}K_b = 9.25$ ), azide ( $\text{p}K_b = 9.28$ ) and benzoate ( $\text{p}K_b = 9.81$ ), in aqueous solution (where potentiometric titrimetry is not applicable), using classical methods for location of the end-point. One disadvantage of the method is that it cannot be directly applied to the titration of very strong bases because they could cause the depolymerization of the polymer. This limitation can be avoided by the formation of a weaker base, by treatment of the solution with,



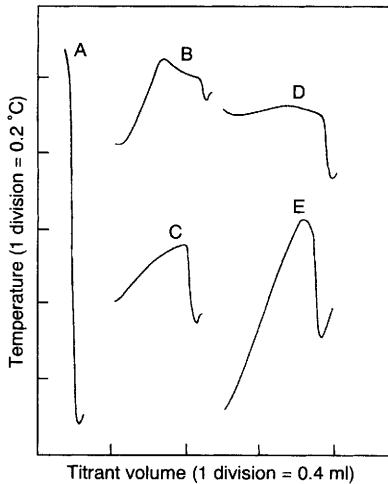
**Fig. 1** Influence of time interval during which the solution of formalin (37% in formaldehyde and 7% in methanol), after diluting 1 + 1 with water, is allowed to stand before titration. Titrant:  $1.055 \text{ mol l}^{-1}$  sodium hydroxide solution. A, 3; B, 28; C, 48; D, 68; E, 88; F, 118; G, 148; H, 178; and I, 208 min. All are blank titrations



**Fig. 2** Influence of the methanol content in formalin solution diluted 1 + 1 on the shape of thermometric titration curves of blank titrations. Titrant:  $0.933 \text{ mol l}^{-1}$  sodium hydroxide solution. Volume of methanol (ml): volume of water (ml): volume of 37% formaldehyde stabilized with 10% of methanol solution (ml); A, 1.0:4.0:5.0; B, 0.9:4.1:5.0; C, 0.8:4.2:5.0; D, 0.7:4.3:5.0; E, 0.5:4.5:5.0; F, 0.4:4.6:5.0; G, 0.3:4.7:5.0; and H, 0.2:4.8:5.0. the titrations were performed immediately after the formalin solution had been added



**Fig. 3** Influence of the nature of the alcohol on the shape of thermometric titration curves of blank titrations. Titrant: 0.933 mol l<sup>-1</sup> sodium hydroxide solution. Volume of alcohol: 5 ml; volume of 37% formaldehyde stabilized with 10% of methanol: 5 ml. A, Butan-1-ol; B, 2-methylpropan-1-ol; C, butan-2-ol; and D, 2-methylpropan-2-ol



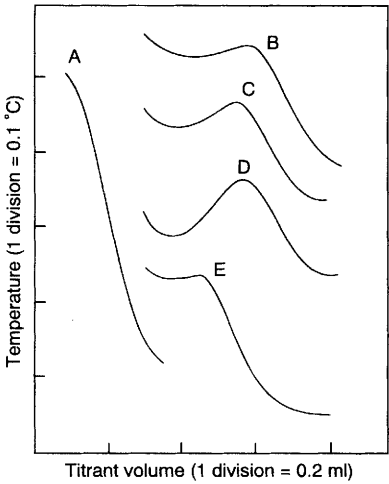
**Fig. 4** Catalytic thermometric titration curves for the titration of acids in formalin solution diluted 1 + 1 with water. Titrant: 0.896 mol l<sup>-1</sup> sodium hydroxide solution. A, Blank; B, phosphoric acid (9.40 mg); C, potassium hydrogenphthalate (20.28 mg); D, succinic acid (26.04 mg); and E, ammonium nitrate (32.12 mg)

for example, acetic acid solution before the formaldehyde solution is added. The titration curve corresponding to the titration of sodium carbonate after the treatment with acetic acid solution is shown in Fig. 5.

**Table 1** Results from the use of formalin in the titrations of acids and bases, and of the use paraformaldehyde in the titrations of soluble and sparingly water soluble acids in the absence and presence of 0.05 mol l<sup>-1</sup> cetrimide

	Moles titrated/ moles present [RSD (%) ]*		
	Formalin (1 : 1)	Paraformaldehyde In the absence of cetrimide	In the presence of cetrimide
<i>Soluble acids—</i>			
Potassium biphtalate	1.01 (1.8)	1.02 (1.0)	—
Phosphoric acid	2.01 (4.2)	1.99 (1.1)	—
Ammonium nitrate	1.01 (6.0)	1.00 (1.5)	—
Succinic acid	2.01 (2.0)	—	—
Boric acid	—	1.03 (1.4)	—
Lysine hydrochloride	—	1.99 (1.5)	—
Arginine hydrochloride	—	0.99 (2.0)	—
<i>Soluble bases—</i>			
Sodium benzoate	1.00 (2.6)	—	—
Sodium acetate	1.04 (1.4)	—	—
Sodium azide	1.00 (2.7)	—	—
Sodium carbonate	1.99 (1.7)	—	—
<i>Sparingly soluble acids—</i>			
Benzoic acid	—	0.77	0.99 (1.5)
Cinnamic acid	—	0.17	0.98 (3.0)
o-Nitrophenol	—	0.62	1.00 (4.4)
Nonanoic acid	—	0.14	1.03 (2.2)

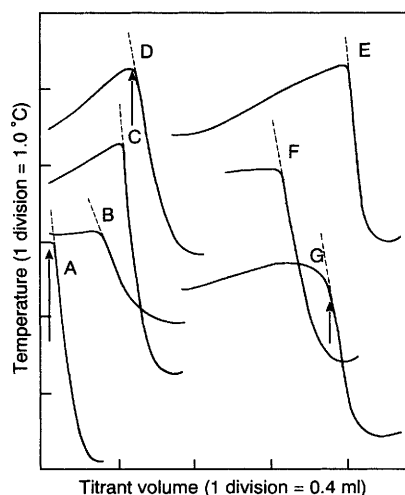
\* Average of three determinations.



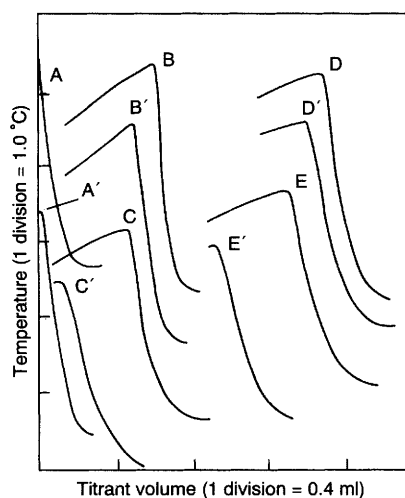
**Fig. 5** Catalytic thermometric titration curves for the titration of bases in formalin solution diluted 1 + 1 with water. Titrant: 0.997 mol l<sup>-1</sup> hydrochloric acid solution. A, Blank; B, sodium benzoate (40.38 mg); C, sodium acetate (47.81 mg); D, sodium azide (16.75 mg); and E, sodium carbonate (11.35 mg)

**Paraformaldehyde as End-point Indicator**

The curves obtained for the titration of acidic substances in aqueous solution, using paraformaldehyde, a water-insoluble polymer of formaldehyde, as a thermometric end-point indicator, are shown in Fig. 6, and the results of these titrations are presented in Table 1. Similar to what happens in the example of formalin solutions, an endothermic end-point is observed. This endothermic effect, which occurs simultaneously with the dissolution of paraformaldehyde, is as a result of the depolymerization of this polymer. The magnitude of the lowering in temperature is dependent on the amount of paraformaldehyde used. Although the results presented in Table 1 are based on a concentration of acids of the order of



**Fig. 6** Catalytic thermometric titration curves for the titration of acids in aqueous solution by employing paraformaldehyde as end-point indicator. Titrant:  $0.972 \text{ mol l}^{-1}$  sodium hydroxide solution. A, Blank; B, boric acid (15.60 mg); C, potassium hydrogenphthalate (74.62 mg); D, phosphoric acid (18.80 mg); E, ammonium nitrate (73.19 mg); F, arginine hydrochloride (18.80 mg); and G, lysine hydrochloride (70.58 mg)



**Fig. 7** Catalytic thermometric titration curves for the titration of some sparingly soluble acids in the presence and absence of a cationic detergent, by employing paraformaldehyde as end-point indicator. Curves A–E: titrand solvent, 10 ml of  $0.04\text{--}0.06 \text{ mol l}^{-1}$  cetrimide. A, Blank; B, benzoic acid (62.23 mg); C, cinnamic acid (63.94 mg); D, *o*-nitrophenol (43.75 mg); and E, nonanoic acid (59.77 mg). Curves A'–E': titrand solvent, 10 ml of water. A', Blank; B', benzoic acid (61.88 mg); C', cinnamic acid (57.46 mg); D', *o*-nitrophenol (49.94 mg); and E', nonanoic acid (53.95 mg)

$0.03 \text{ mol l}^{-1}$ , the method can be applied to concentrations in the range  $0.1\text{--}0.001 \text{ mol l}^{-1}$ .

The titration curves for the titration of some sparingly water-soluble acids, in the presence of cationic detergents are, presented in Fig. 7, and the results of these titrations are presented in Table 1. Shukla and Meites<sup>9</sup> have shown that

such determinations, which are unsatisfactory by potentiometric titrimetry, can be performed by conventional thermometric titrimetry. In this work, it is shown that these titrations are also possible by CTT.

## Conclusions

From the analytical viewpoint, paraformaldehyde presents some advantages in relation to formalin solution as an end-point indicator for the titration of acids in aqueous solutions. The titration curves obtained by use of paraformaldehyde are more easily reproducible than those in formalin solutions. Another point to be considered is that, with paraformaldehyde, for the amount used the change in temperature at the end-point is about five times greater than with formalin.

The titration of boric acid in aqueous solution is generally mentioned as an example where conventional thermometric titrimetry is superior to potentiometric titrimetry. In these instances, the potentiometric titration curves do not present a defined inflection at the end-point. It was shown in this work that it is possible to titrate boric acid, or other weak acidic substances in aqueous solution, by CTT with use of paraformaldehyde as an end-point indicator. Another point worth mentioning is that, in CTT, the temperature change during the course of a titration is one to two orders greater than that in the conventional technique. Therefore, no serious precautions need be taken to avoid the exchange of heat with the environment or with the temperature difference between titrand and titrant.

Finally, it is interesting to remember that formalin and paraformaldehyde are unique examples of endothermic end-point indicators. In addition, formalin solution is a unique example of a thermometric indicator that can furnish endothermic or exothermic end-points, depending on the concentration of methanol in the solution.

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