STUDIES ON THERMOMETRIC TITRATION

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PREFACE

Determination of heats of reaction is among the oldest arts in quantitative chemistry. Thermometric titration, however, is a relatively new technique in the field of modern analytical methodology. The basic principle is simple. A solution is titrated with a suitable reagent under effectively adiabatic conditions, and the change of temperature is recorded simultaneously.

The crucial difference between thermometric titrations and most titrimetric methods of analysis is inherent in the fact that the shape of thermometric titration curves is determined by the heat of the reaction *in toto*. In contradistinction, potentiometric (and similar) titration curves depend solely on the relevant equilibrium constants which account also for the color change behavior of indicators normally used for visual end-point detection. Thus, new information which can not be obtained by potentiometric titration can be obtained by judicious interpretation of thermometric titration curves.

Thermometric titrations are successfully applied to the investigations of the formation of polyanions of molybdenum(VI), tungsten(VI), vanadium(V), and chromium(VI). Thermometric titrations using differential thermistor are also applied to the determinations of molybdenum compounds and amines.

The present dissertation contains the studies on thermometric titration which have been pursued at Nagoya University under the direction of Professor Tsugio Takeuchi during 1969 - 1973.

The author wishes to express his gratitude to Professor Tsugio Takeuchi for his pertinent direction and constant encouragement throughout this work.

He should like to express his thanks to Dr. Mitsuru Yamazaki for his valuable discussions in the thermometric titrations using differential thermistor.

Thanks are also due to the following members for an offer of pleasurable the author's place of work: Dr. Y.Suzuki, Mr. K.Matsumoto, Mr. T.Tanaka and other investigators in the Takeuchi's Laboratory.

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PART I

INTRODUCTION

INTRODUCTION

Thermometric titration seems to be useful not only for the determination of a substance in a solution, but as a technique to follow the chemical reaction proceeding in the solution and to estimate the chemical species occo~~u~~rring the process. It will be more powerful when the data obtained by this method are combined with those by other methods such as potentiometry, conductometry, and spectrophotometry. However, in the thermometric titration it is desired to obtain precise titration curves having delicate inflections and further more to estimate the heat of reaction from the curves. It, therefore, is necessary to eliminate the effect of the heat of dilution accompanied with the titration and to minimize the change of the heat capacity of the vessel and its content; thus an accurate and precise titration curve would be obtained. To this end the present author devised a thermometric titrator of new type which has two adiabatic titration vessels, one for a test solution of the same composition except for the substance to be tested. Into both vessels, each containing its proper solution, a titrant solution is introduced from two injection syringe type automatic burettes, simultaneously and separately, at the same rate. A thermistor inserted in the sample vessel is connected with another in the reference vessel as to compensate each other, therefore when the temperature in the individual vessels is identical, the current is zero at balance. Thus, the heat of dilution which is evolved by the addition of a titrant in higher concentration can also be compensated on the indicating scale or the pen-recorder, and a net thermal change can only be observed. Furthermore, the change of heat capacity of the vessel and its content would be an important factor to obtain a precise titration curve; therefore it should be minimized by keeping the following condition as the volume of a titrant before the finish of a titration has to be less than one per cent of the volume of a solution to be titrated; the concentration of the titrant should be adjusted to satisfy the above requirement. Needless to say, the heat capacity of both titration vessels should be identical, and the vessels of such property must be chosen.

The author has been interested in the formation of polyanions in the course of mineral acid titration of a neutral solution containing a salt of an oxyanion such as molybdate, tungstate, orthovanadate, metavanadate, and chromate. A number of investigators have approached this problem with the aid of various physical and chemical methods. For example, the polymerization of molybdate has been investigated by potentiometric and conductometric titrations[1], cryoscopic titration[2], polarography and amperometry[3], Raman spectroscopy and ultracentrifugation[4], and ultraviolet spectrophtometry[5], and isopolymolybdate anions such as $Mo_4O_{13}^{2-}$, $Mo_6O_{21}^{6-}$, $Mo_7O_{24}^{6-}$, and $Mo_8O_{26}^{4-}$ have been reported as the polymerization products in the course of acidification. Jahr and Fuchs[6] have reviewed the method applicable for the study of the formation of polyanions containing molybdenum, tungsten, and vanadium respectively, and also listed the polymerization products. However, their review did not include thermometric titrations, and it may be said that this method has never been applied sufficiently to investigations of the formation of polyoxyanions.

Though thermometric titration is widely used for investigation of complexation reactions, the results have to be confirmed by other methods such as potentiometric or conductometric titration[7]. Precise thermometric titrations have been used alone to determine simultaneously free energy change(ΔG) and enthalpy change(ΔH), by Christensen *et al.*[8-11], who interpreted the titration curves with aid of a computer.

Recently, however, Cabani and Gianni[12] showed that these simultaneous determination techniques seem to be limited in application to only simple reactions. The lack of reliability of the method may be due to the difficulty of obtaining a sufficiently accurate titration curve, since in the classical thermometric titrator the heat of dilution and the change of heat capacity during the titration had serious effects on the titration curve. Now, with a thermometric titrator of new type, the thermometric titration method can be used alone not noly for determination of the end-point in titrations but also for elucidation of complicated processes in a reaction; that seems to be a modern aspect of analytical chemistry.

A thermometric titrator having two titration vessels and two burettes was first devised by Tyson *et al*[60]. In their apparatus the temperature-sensing device consisted of four thermistors connected in parallel. I have tried to make such a device, but failed to prepare two identical sets of four thermistors having the same resistance temperature response. Hence, only two thermistors of the same resistance temperature response were chosen and used in our apparatus. Tyson *et al.*[60] used polyethylene cups as titration vessels, in which significant losses of heat could not be prevented during the titration. They recommended the rapid injection of titrant into the vessel, *e.g.*, within 10 sec, to obtain a titration curve of good shape. I used a Dewar flask as the titration vessel to avoid heat loss, and the titration could be achieved adiabatically even at a reduced rate of titration for relatively slow reactions.

The thermometric titration using differential thermistor was first carried out by Takeuchi and Yamazaki[55]. The end-point of the thermometric titration is usually determined as the point of intersection after extrapolation of the titration curve before and after the inflection point. However, the reproducibility is invariably poor, particularly when the inflection of the curve is not sharp. I employed a differential thermistor probe in orde to carry out more precise titrimetric determinations of molybdenum compounds and amines.

PART II

THERMOMETRIC TITRATION IN INVESTIGATION OF THE FORMATION OF POLYANIONS OF MOLYBDENUM(VI), TUNGSTEN(VI), VANADIUM(V), AND CHROMIUM(VI)

COMPARISON OF THERMOMETRIC AND POTENTIOMETRIC TITRATION CURVES

Summary

A new twin-cell thermometric titrator has been devised and used for thermometric titration of solutions of sodium molybdate, sodium tungstate, sodium orthovanadate, ammonium metavanadate, and potassium chromate with perchloric acid. The thermometric titration curves were compared with corresponding pH-titration curves for elucidation of the reactions occurring in the titrations. Thermometric titrimetric methods have been developed for the determination of tungsten, vanadium and chromium.

Introduction

I used the new titrator to obtain thermometric titration curves for sodium molybdate, tungstate and orthovanadate, ammonium metavanadate and potassium chromate with perchloric acid. The pH-titration curves for the same systems were also determined, and the reaction processes deduced from results obtained by both methods. Tungstate, vanadate, and chromate were found to give thermometric titration curves with inflections at a fixed mole ratio between the salts and the acid, and therefore can be determined by titration with a standard acid solution.

Experimental

Apparatus

Thermometric titrator. The apparatus was similar to a thermometric titrator TMT-1A supplied commercially by TOA Electronic Co. Ltd., Tokyo, except for titration system. The titration system was improved by substituting two syringe-type automatic injection burettes for the original burette. The essential features of the apparatus are shown in Fig. 1. The titration vessels were 50-ml Dewar flasks. The titration rate was 0.2ml/min.

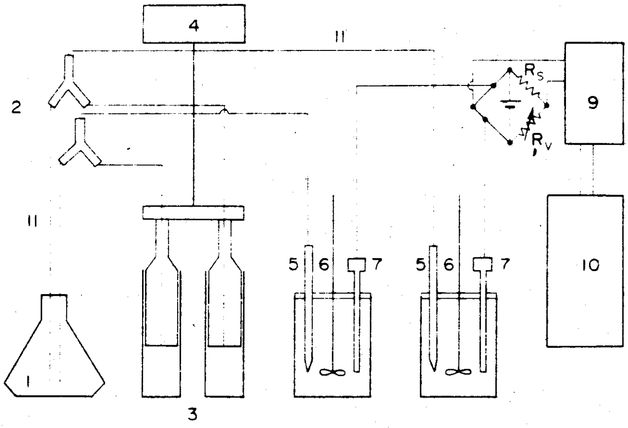


Fig. 1. Thermometric titration apparatus.
1 Titrant vessel; 2 three-way taps; 3 injection syringe burettes; 4 synchronous burette motor; 5 burette tips; 6 stirrer; 7 thermistor (R at 25 C = 20 kΩ, B = 2800 ± 10 K, time-constant = 0·3 sec); 8 adiabatic titration vessels (Dewar); 9 amplifier; 10 recorder; R_s = 20 kΩ; R_v = variable resistor; 11 Teflon tube.

Potentiometric titration. A Metrohm Potentiograph E336 and glass electrode were used.

Reagents

Perchloric acid. Reagent grade perchloric acid(70 %) was diluted with water to an appropriate concentration, and standardized with sodium carbonate solution as usual.

Sodium molybdate solution, 0.5M. Standardized with 8-hydroxyquinoline[13].

Sodium tungstate solution, 0.5M. Standardized as for the molybdate.

Sodium vanadate solution, 1.0M. Standardized volumetrically[14].

Ammonium vanadate solution, 0.1M. Standarized volumetrically[14].

Potassium chromate solution, 1.0M. Standardized volumetrically.[14]

All salts used were Wako Chemicals'extra pure grade. Samples from two separate batches were used for the sodium tungstate, metavanadate and chromate, potassium tungstate and chromate, and ammonium metavanadate. Samples from three separate batches of sodium orthovanadate were used. The tungstate were checked gravimetrically as tungstic oxide[15], and the vanadates and the chromates volumetrically by the method of Kolthoff and Sandell[14].

Procedure

The two titration vessels were charged, one with 10 - 30ml of sample solution and the other with an equal volume of reference solution, the solutions having been brought to thermal equilibrium with the surroundings. All titrations were carried out at room temperature (25± 0.5°C). The titrant concentration was 90 - 100 times that of the titrand, so that the reaction was complete on addition of about 0.1 - 0.3ml, and thus the volume change and consequent heat capacity change were kept to a minimum. The cover with its attached thermistors, stirrers, and burette tips was fitted, and when the thermistor-bridge recorder gave a steady trace the synchronous burette motor was started to perform the titration. A suitable bridge sensitivity was chosen by trial and error. The trace was 10 - 30cm long for each titration, so the titration volumes could be measured to three significant figures.

The pH-titrations were carried out by successive addition of 0.05ml portions of perchloric acid to 100ml of salt solution.

To obtain precise titration curves at high molar ratios of the added acid to salt, the acidified salt solutions were titrated thermometrically and potentio-

metrically with perchloric acid.

Results and discussion

Throughout this paper the inflection point of the titration curve is called the Z-value,*i.e.,* the molar ratio of added perchloric acid to neutral salt taken initially. Both thermometric and potentiometric titrations were performed, for comparison purposes.

Acidification of sodium molybdate solution.

The pH-titration curves were identical with those reported by others[1], the Z-value fell between 1.2 and 1.5 for titration of 0.2 - 0.04M sodium molybdate and this value agrees with that found by other researchers[1,16].

The thermometric titration curves are shown in Fig.2. Three distinct break-points can be observed on the titration curve of 0.2M sodium molybdate(Fig.2A), but only one the pH-titration curve. The inflections have Z-values of 1.14, 1.43 and 2.00, respectively. For molybdate solution in lower concentration($5x10^{-3}$M) only one inflection point was observed on the thermometric curve(Fig.2C), and the Z-value was 1.50. The pH-titration curve had no inflection at all.

These results show thermometric titration to be

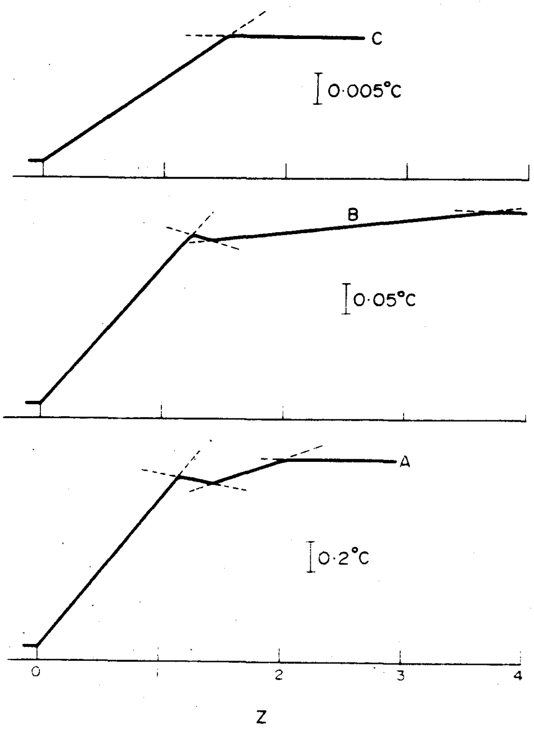


Fig. 2. Thermometric titrations of sodium molybdate with perchloric acid. [Na_2MoO_4]: A 0·2250M : B 0·0428M : C 0·00535M. The ordinate is relative heat change during the titration.

superior to pH-titration. The variation of the Z-values with initial concentration of molybdate will give much inflection about the polymerization of molybdate and the chemical species appearing during the acidification. The process of the acidification of molybdate can be interpreted as follows from the three inflections of the thermometric titration and from the results of other investigator[1-5]. From Fig.2, it can be seen that the first inflection is shifted to higher Z-values with decreasing initial concentration of molybdate. When the initial sodium molybdate solution is about 0.2M the first product is the heptamolybdate:

$7MoO_4^{2-} + 8H^+ = Mo_7O_{24}^{6-} + 4H_2O$; calculated Z-value 8/7 = 1.143(obserbed=1.14). From 0.005M molybdate, the octamolybdate is the first product formed:

$8MoO_4^{2-} + 12H^+ = Mo_8O_{26}^{4-} + 6H_2O$; calculated Z-value 12/8=1.50(observed=1.50). The second inflection is given by; $Mo_7O_{24}^{6-} + 2H^+ = H_2Mo_7O_{24}^{4-}$; calculated Z-value 10/7=1.43(observed 1.43), and the third by ;

$8H_2Mo_7O_{24}^{4-} + 32H^+ = 7H_4Mo_8O_{26} + 10H_2O$; calculated Z-value 112/56=2.00(observed 2.00). In Fig.2B, the Z-value of the second inflection is lower than the calculated value. This seems to indicate, as mentioned above, that part of the heptamolybdate was converted directly into octamolybdate, without intermediate protonation.

Acidification of sodium tungstate solutions.

The pH-titration curves for 0.005 - 0.5M sodium tungstate all have a single Z-value of 1.2, but the inflection point becomes difficult or impossible to observe, as the tungstate concentration of the starting solution decreases. For sodium tungstate concentrations $>$ 0.01M a light yellow precipitate formed during the titration. Thermometric titration curves are shown in Fig.3. Three inflections were observed for 0.2M sodium tungstate the second of which was attributed to the heat of precipitation, and only two were observed for 0.005M sodium tungstate. The Z-values of the two inflections were 1.17 and 1.50. The polymerization can be elucidated as described below and the fixed Z-value in thermometric titrations can be applied for the determination of tungstate. Typical results are shown in Table 1.

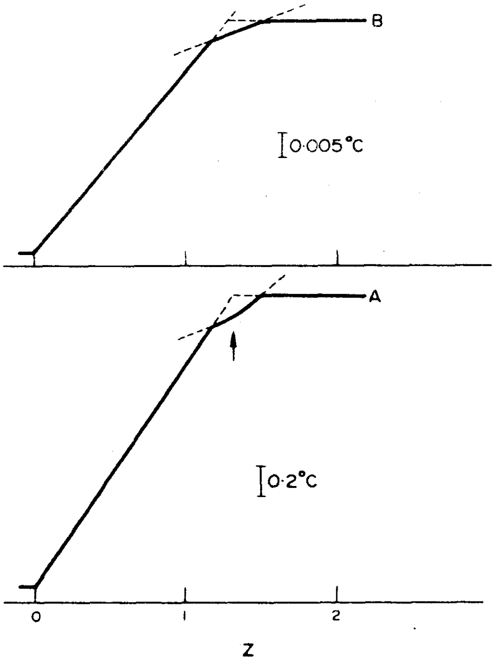


Fig. 3. Thermometric titrations of sodium tungstate with perchloric acid. $[Na_2WO_4]$: A 0·2030M; B 0·00502M.

Table 1. Comparison of results for tungsten determination. (Each value is the average of 50 determinations)

Compound	Sample No.	Tungsten, %		
			Thermometric	
		Gravimetric[17]	1st inflection	2nd inflection
Sodium tungstate	1	55·5 (0·43)*	55·7 (0·15)*	55·4 (0·62)*
	2	55·6 (0·30)	55·7 (0·16)	55·4 (0·68)
Potassium tungstate	1	50·7 (0·65)	50·6 (0·14)	50·5 (0·48)
	2	50·6 (0·50)	50·6 (0·17)	50·5 (0·59)

* Coefficient of variation = $100[\Sigma(x_i - \bar{x})^2/n]^{1/2}/\bar{x}$ %.

From the thermometric titration curves and results obtained by other methods[17-19] I can postulate the first inflection as corresponding to
$6WO_4^{2-} + 7H^+ = HWO_6O_{21}^{5-} + 3H_2O$;calculated Z-value 7/6=1.167(observed 1.17) and the second as
$HW_6O_{21}^{5-} + 2H^+ = H_3W_6O_{21}^{3-}$; calculated Z-value 9/6=1.500 observed 1.50).

Acidification of sodium orthovanadate solutions

The pH-titration curves had one inflection at a Z-value of 1.0 irrespective of the initial concentration of vanadate initially taken. A second inflection was observed for 0.2 and 0.08M vanadate but not 0.02M vanadate.

Thermometric titration curves are shown in Fig.4. Three inflections with Z-values 1.00, 1.50 and 3.0 were found for o.2M vanadate but only one at Z-value 1.00 for the 0.02M solution. The Z-value of the first inflection point of both the types of titration curve corresponds to protonation of the vanadate ion[20,21].
$VO_4^{3-} + H^+ = HVO_4^{2-}$; calculated Z-value 1.00(observed 1.00). The second inflections of both titration curves are dependent on the concentration of vanadate and the reaction is as follows[20,21].
$2HVO_4^{2-} + H^+ = HV_2O_7^{3-} + H_2O$; calculated Z-value 3/2= 1.50(observed 1.50). The third inflection could

correspond to:

$5HV_2O_7^{3-} + 15H^+ = H_6V_{10}O_{28}$; calculated Z-value 30/10= 3.00(observed 3.0).

Howarth *et al.*,[21] on the basis of their NMR observations, concluded that the dimerization was acid-catalysed, and rapid for 0.125M vanadate. In my work the dimerization was rapid for 0.2M vanadate but seemed to occur scarcely at all in 0.02M vanadate since the second inflection which indicates the initiation of the formation of $H_6V_{10}O_{28}$ could not be observed at all for the 0.02M solution.

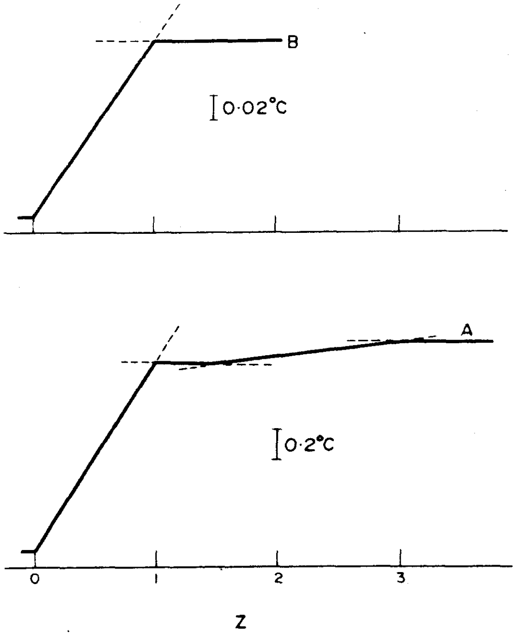


Fig. 4. Thermometric titrations of sodium orthovanadate with perchloric acid. $[Na_3VO_4]$: A 0·2466*M*: B 0·0247*M*.

Acidification of ammonium metavanadate solutions

The $V_4O_{12}^{4-}$ ion is said to be already present in the test solution[22-24]. The pH-titration curves give a single inflection point at a Z-value of 0.4 for all concentrations of ammonium metavanadate.

Thermometric titration curves are shown in Fig.5 and have three inflections at Z-values of 0.40, 1.00 and 2.00, the third being less clear-cut. The thermometric titration curve for 0.02M ammonium vanadate has only one inflection at a Z-value of 0.4. The first inflection seems to be independent of the concentration of vanadate, but the others not.

Vanadate in 0.005 - 0.5M orthovanadate and in 0.01 - 0.1M metavanadate can be determined by thermometric titration since the Z-values of the first inflections are independent of the initial vanadate concentration. Table 2 shows typical results.

From the thermometric titration curves and the results of other investigators[20,22] the course of acidification of metavanadate appears to be

$5V_4O_{12}^{4-} + 8H^+ = 2V_{10}O_{28}^{6-} + 4H_2O$; calculated Z-value 8/20 =0.400(observed 0.40) followed by

$V_{10}O_{28}^{6-} + 6H^+ = H_6V_{10}O_{28}$; calculated Z-value 20/20 =1.00(observed 1.00) and

$H_6V_{10}O_{28} + 10H^+ = 10VO_2^+ + 8H_2O$; calculated 40/20=2.00

(observed 2.0).

This last step may go in two stages: $H_6V_{10}O_{28} = 5V_2O_5 + 3H_2O$ followed by $V_2O_5 + 2H^+ = 2VO_2^+ + H_2O$. The formation of V_2O_5 is independent of the hydrogen ion concentration but dependent on that of vanadate[20]. Therefore its formation would be rapid in 0.1M solution, but slow in 0.01M solution; the second and the third inflections would consequently not be observed for the more dilute solution.

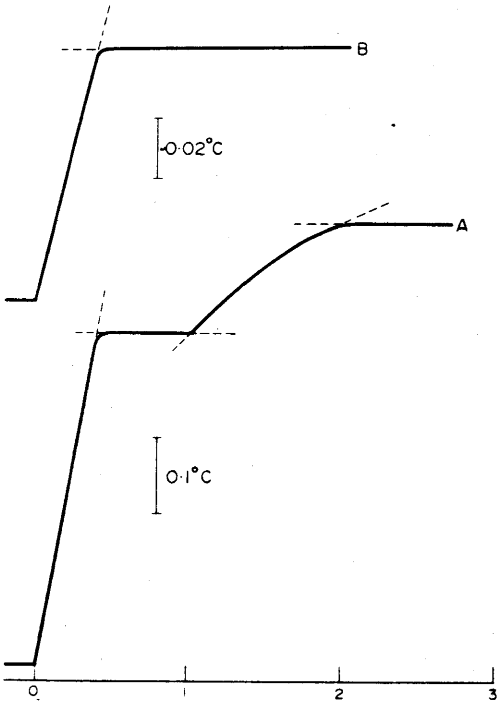


Fig. 5. Thermometric titrations of ammonium metavanadate with perchloric acid. $[NH_4VO_3]$: A 0·1000M; B 0·0200M.

Table 2. Comparison of results for vanadium determination. (Each values is the average of 50 determinations)

Compound	Sample No.	Vanadium, %	
		Volumetric[1,2]	Thermometric
Sodium orthovanadate	1	23·7 (2·9)*	24·6 (1·7)*
	2	24·2 (2·5)	25·1 (1·0)
	3	24·0 (2·7)	24·6 (1·3)
Ammonium metavanadate	1	43·1 (0·88)	43·5 (0·24)
	2	42·4 (0·80)	43·2 (0·35)
Sodium metavanadate	1	41·2 (1·1)	41·7 (0·31)
	2	40·4 (1·1)	41·4 (0·45)

* Coefficient of variation.

Acidification of potassium chromate solutions

The pH-titration curves and the thermometric titration curves have a single inflection at a Z-value of 1.0 in 0.05 - 1.0M potassium chromate solutions. As the Z-value for chromate titration is always 1.00, chromate can be determined by thermometric titration. Results are shown in Table 3. The thermometric titration confirms the condensation of chromate to form dichromate.

Table 3. Comparison of results for chromium determination. (Each value is the average of 50 determinations)

Compound	Sample No.	Chromium, %	
		Volumetric[1,2]	Thermometric
Potassium chromate	1	26·7 (1·0)*	26.7 (0·10)*
	2	26·7 (1·0)	26·7 (0·11)
Sodium chromate	1	31·8 (1·0)	32·0 (0·32)
	2	31·6 (1·3)	31·7 (0·30)

* Coefficient of variation.

The pH-change in the pH-titration is based on ΔG, but the temperature change in the thermometric titration depends on ΔH. From $\Delta G = \Delta H - T\Delta S$, comparison of the two titration curves gives some idea of whether the reaction mechanism is mainly influenced by ΔH or ΔS. For example, in the acidification of tungstate the process before the first inflection seems to have large ΔH and ΔS, whereas the process between the first and the second inflections has large ΔH but rather small ΔS.

INVESTIGATIONS OF POLYMERIZATION OF SODIUM MOLYBDATE BY THE THERMOMETRIC TITRATION

Summary

In order to clarify the polymerization process of molybdate, thermometric titrations were attempted for neutral sodium molybdate solution with mineral acids (hydrochloric acid and perchloric acid) and for acidified sodium molybdate solution with sodium hydroxide. From the inflections of the titration curve, the polymerization reaction was found to proceed from monomeric molybdate to heptamolybdate ion without any intermediate steps and this polyanion was then protonated to be $H_2Mo_7O_{24}^{4-}$ *followed by formation of octamolybdate ion, when the initial concentration of the monomeric molybdate was high. On the other hand, in the initial low concentration of the reaction proceeded directly to the octamolybdate. When a large amount of a neutral salt was present in the solution the first-formed product was only heptamolybdate in any initial concentration of monomeric molybdate. The process,* $MoO_4^{2-} \longrightarrow Mo_7O_{24}^{6-} \longrightarrow H_2Mo_7O_{24}^{4-} \longrightarrow HMo_8O_{26}^{3-} \longrightarrow H_4Mo_8O_{26}$*, was proposed by the present author. The heats of polymerization reaction were measured in each step.*

Introduction

Lindqvist has reviewed the works upon to 1950[25], subsequently has certified the existence of the ions $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$ in crystalline ammonium molybdate by X-ray crystallographic measurement[26], and has also obtained an evidence leading to an assumption that the reaction taking place upon acidification of alkali molybdate solution[27] is $MoO_4^{2-} \rightarrow Mo_7O_{24}^{6-} \rightarrow Mo_8O_{26}^{4-} \rightarrow$ larger complex ions. Similar results have also been reported by a cryoscopic titration work of Wiese[2], and a spectrophotometric study of Halasz *et al.*[28]

Sasaki *et al.*[29] found that $Mo_7O_{24}^{6-}$ is the first polymeric species to be formed on acidification of alkali molybdate solution, that there are more highly protonated heptamers($HMo_7O_{24}^{5-}$ and $H_2Mo_7O_{24}^{4-}$) increasing acidity, and that there are two monomeric species($HMoO_4^{1-}$ and H_2MoO_4) at low concentration of molybdate and low acidity of the solution.

The equilibrium constant of each step has been reported by Sasaki *et al.*[29-31] at 25°C in 3M sodium perchlorate solution, by Baldwin *et al*[32] in 1M magnesium perchlorate solution, and by Haeriger *et al*[33] in sodium chloride solutions.

Rate constant of the polymerization reaction has been estimated[34] to be in the order of at least 10^5 liters $mole^{-1}$ sec^{-1}.

Recent studies by spectrophotometry indicate that the reaction taking place upon acidification of alkaki molybdate solution may consist of the following successive processes[5];

$MoO_4^{2-} \longrightarrow Mo_7O_{24}^{6-} \longrightarrow H_2Mo_7O_{24}^{5-} \longrightarrow Mo_8O_{26}^{4-} \longrightarrow MoO_2^{+}$.

On the other hand, in the study of the reaction as a function of the pH during the titration, the inflection points of the titration curve have been found depending upon the initial concentration of molybdate[1]. The case of this phenomena has yet been unaccounted for, because it is still ambiguous whether $Mo_7O_{24}^{6-}$ or $Mo_8O_{26}^{4-}$ is the predominant species, whether both of them can simultaneously be in the solution, and whether they are able to be present among with the protonated species.

The author had previously investigated the acidification process of sodium molybdate, sodium tungstate, sodium orthovanadate, ammonium metavanadate, and potassium chromate by means of thermometric titration and potentiometric titration with perchloric acid[35]. Among these salts, sodium molybdate showed an anomalous behavior as Z-value, molar ratio of the acid added to the salt, of the inflections appearing on the titration curve varies with the initial concentration of sodium molybdate taken in a test solution. I. had proposed an assumption to account for the phenomenon. It is that when the sodium molybdate solution is of its concentration of 0.2 M the first-formed product is the heptamolybdate according to the reaction I.

$$7\ MoO_4^{2-} + 8\ H^+ = Mo_7O_{24}^{6-} + 4\ H_2O \tag{I}$$

For the concentration 0.04 M, both heptamolybdate and octamolybdate can be existing simultaneously, and for the concentration 0.005 M, the octamolybdate is the first product according to the following reaction.

$$8\ MoO_4^{2-} + 12\ H^+ = Mo_8O_{26}^{4-} + 6\ H_2O \tag{II}$$

When the concentration is above 0.04 M, the second step corresponds to the protonation of the heptamolybdate (reaction III), and the third step is the condensation of the heptamolybdate into the octamolybdate and the protonation of the latter (reaction IV).

$$Mo_7O_{24}^{6-} + 2\ H^+ = H_2Mo_7O_{24}^{4-} \tag{III}$$

$$8\ H_2Mo_7O_{24}^{4-} + 32\ H^+ = 7\ H_4Mo_8O_{26} + 10\ H_2O \tag{IV}$$

In order to verify the above assumption, further precise investigations on the acidification process of sodium molybdate were carried out by the thermometric titration, with the aid of the ultraviolet spectrophotometry reported by Pungor *et al.*[5]. A thermometric titrator of a new design as described in detail in the previous paper[35] was used.

Experimental

Apparatus

A thermometric titrator with an electronic recorder, manufactured by TOA Electronic Co. Ltd., Tokyo, was employed through this work. The constitution and the advantage of this apparatus have already been described in the previous paper[35]. *All spectrophotometric measurements were carried out by an automatic SHIMADZU ultraviolet spectrophotometer. Differece spectrum of the acidified molybdate solution against neutral monomeric molybdate was measured at 225 nm. Silica microcuvettes of path length 1.0 - 0.02 mm were used.*

Reagents

Sodium molybdate soluiton. Sodium molybdate dihydrate of the reagent grade was dissolved in water to make a 0.5M solution and this solution was diluted to an appropriate concentration for use. The concentration was determined gravimetrically by weighing precipitate of molybdenum 8-hydroxyquinolinate as usual; the content of the cationic species was examined by passing the solution through a column of Amberlite ITA-401 in hydroxide form and by titrating the effluent with a standard hydrochloric acid solution.

Dilute hydrochloric acid. A 35% reagent grade hydrochloric acid was diluted with to an approproate concentration; the solution was standardized against a standard sodium carbonate solution.

Dilute perchloric acid. A 70% reagent grade perchloric acid was diluted with water to an appropriate concentration; the solution was titrated with a standard sodium hydroxide.

Sodium hydroxide solution . Sodium hydroxide of the reagent grade was used. The solution was titrated with a standard solution of hydrochloric acid.

Other reagents such as lithium chloride, sodium chloride, potassium chloride, and sodium perchlorate were all of the reagent grade, and these were used without further purification.

Experimental procedure

The thermometric measurments were carried out in the concentration range of sodium molybdate of 2×10^{-1}M to 4×10^{-3}M. All titrations were performed with the solution that had been put aside for a long time till their thermal equilibrium with surrounding was maintained perfectly; the temperature of the chamber of the apparatus was kept at 25°C and that of the laboratory room was also the same. In order to obtain good results in every reaction process and to derive the heat of reaction from the above results, careful manipulation in the thermometric titration should be necessary, especially by considering the reaction rates and the addition rates of a titrant. The titration rates were

1ml/12min. and 1ml/6min.. For obtaining the precise titration curves at high Z-values, the acidified sodium molybdate solutions of various Z-values were titrated with acids or sodium hydroxide; Z-values are 0.5, 1.0, 1.4, and 1.8. The concentration of the titrant was kept to be about 100 times that of the titrand; therefore, the volume change, that is the change of the heat capacity of the content, be also to be minimized. A thermogram is about 200.0 to 300.0mm long for each titration; the volume of the titre could be made to three significant figures and a fourth figure is uncertain. It was writted by the subscript in Z-value.

In order to calculate the calorimetric values from the experimental results, the thermometric instrument was accurately calibrated for heat measurment by using the precision heater. The heater consisted of a Teflon-sealed platinum film resistor(100.0 ohm at 25^{o}C) and coulometric current was passed through the resistor from a source manufactured by OKANO manufactry Co., Osaka; heat of reaction in each step was estimated from the thermogram obtained by the extrapolation method[36]*, the values of calory estimated by such manner was accurate to within 3%.*

Results and discussion

Polymerization process

All experiments in this section were carried out in 1.0M lithium chloride solution to keep constant ionic strength and in the Z-value range up to 2. The shapes of the thermometric titration curves of sodium molybdate with hydrochloric acid were similar to those described previously[35]. The data obtained the titrations of molybdate solution of various concentrations, from 2.140x 10^{-1}M to 4.280 x 10^{-3}M, are summarized in Table 1, together with coefficient of variation(%). From data of coefficients of variation, the Z-values are regarded as reliable data. It can be seen from Table 1 that the first inflection is shifted to higher Z-values with the decreasing concentration of molybdate to be titrated. The position finally reaches at the constant value of Z = 1.50. On the basis of the fact it can be said that when molybdate concentration is above 1.71 x 10^{-1}M the heptamolybdate is the first product according to reaction I. In the concentration range between 1.50 x 10^{-1}M and 1.07 x 10^{-2}M, both of heptamolybdate and octamolybdate can be existing simultaneously. When the concentration is lowered below 8.56 x 10^{-3}M, the octamolybdate becomes the first-formed product. This interpretation is supported experimentally by the spectrophotometric measurements of acidified molybdate solution against neutral monomeric molybdate solution at 225nm similary to Pungor *et al*'s method. In the first step of the concentration above 1.71 x 10^{-1}M the octamolybdate could not be observed, but below 1.50 x 10^{-2}M it could be observed.

Table 1 Results of the thermometric titration of sodium molybdate solution of various concentrations with hydrochloric acid in 1.0M LiCl. Z-value= number of moles of acid added per mole of MoO_4^{2-}.

Concentration	Z-value*		
of Mo(M)	1st inflection	2nd inflection	3rd inflection
$2.140x10^{-1}$	1.14_3(0.6)**	1.43_0(0.6)**	2.00_4(0.7)**
$1.926x10^{-1}$	1.14_3(o.6)	1.43_0(0.6)	2.01_5(0.8)
$1.712x10^{-1}$	1.14_4(0.6)	1.42_9(0.6)	2.03_4(0.9)
$1.498x10^{-1}$	1.14_9(0.6)	1.42_6(0.7)	2.10_3(1.3)
$1.284x10^{-1}$	1.15_0(0.6)	1.42_4(0.7)	2.10_6(1.5)
$1.070x10^{-1}$	1.16_8(0.8)	1.42_0(0.8)	2.3(5.5)
$8.560x10^{-2}$	1.20_0(1.0)	1.41_3(0.8)	2.6(5.5)
$6.560x10^{-2}$	1.22_8(1.2)	1.40_7(1.1)	2.8(7.2)
$4.280x10^{-2}$	1.24_3(1.4)	$1.4o_2$(1.3)	3.6(8.3)
$2.140x10^{-2}$	1.34_2(1.6)	1.39_8(1.4)	———
$1.926x10^{-2}$	1.36_3(1.6)	———	———
$1.712x10^{-2}$	1.37_4(1.7)	———	———
$1.428x10^{-2}$	1.37_9(1.8)	———	———
$1.284x10^{-2}$	1.40_0(1.8)	———	———
$1.070x10^{-2}$	1.43_5(1.9)	———	———
$8.560x10^{-3}$	1.49_6(2.0)	———	———
$5.350x10^{-3}$	1.49_9(2.0)	———	———
$4.280x10^{-3}$	1.50_0(2.0)	———	———

* Each Z-value is the average of 7 runs.

** Coefficient of variation(%).

To make sure the reaction III and IV, spectrophotometric measurements were carried out in the solution corresponding to the second step and third step. In the second step the octamolybdate could not be observed, but in the third step it could be observed.

Spectrophotometric measurements made of 3min., 30 min., and 3 hours, respectively, after each aliquot of hydrochloric acid solition added into a molybdate solution. Each absorbance remained unaltered. All Z-values were not influenced by the changes in the titration rates.

Pungor and Halasz[5] have reported that even at a concentration of 1 x 10^{-3}M of sodium molybdate, the first product was the heptamolybdate, and when the Z-value become below 1.43 the behavior of this system seemed to be independent of the concentration of molybdate over the range between 1 x 10^{-1}M and 5 x 10^{-4}M. Their conclutions have been based on their spectrophotometric measurments of the system in which ionic strength is not kept constant. The distinction between their results and mine may be due to a difference in the experimental condition.

Depolymerization process

In order to confirm the polymerization process reversely, a back titration of a solution containing the polyanions with sodium hydroxide solution was carried out. In this case the solutions of sodium molybdate of $2.290 \times 10^{-1}M$ to $1.712 \times 10^{-1}M$ in lithium chloride was made acidic by adding an excess of hydrochloric acid.

A titration curve is shown in Fig.1, where the titration was carried out with sodium hydroxide for a solution of $1.712 \times 10^{-1}M$ sodium molybdate and hydrochloric acid of 2.232 times the molarity of the molybdate. In Fig.1, four inflections can be found on the curve and after deducting the volume of sodium hydroxide to be required for the excess of the acid added, the inflection points are corresponding to the OH/Mo ratio(that is called P-value) of each step of the depolymerization, that is the first 0.375, the second 0.571, the third 0.857 and the fourth 2.00. It is also interesting that no inflection can be seen on the titration curve before the first inflection appears. This suggests that heat of neutralization between hydrochloric acid existing excess and sodium hydroxide and that molybdic acid, probably $H_4Mo_8O_{26}$, and the same alkali are apparently equal to each other.

From the fact and P-value obtained above, it can be proposed that in the range of P=0 to P=0.375 the following reaction might proceed:

$$H_4Mo_8O_{26} + 3\ OH^- = HMo_8O_{26}^{3-} + 3H_2O \qquad \text{———} \quad (V)$$

As the slope of the titration curve between P=0.375 and P=0.517 is rather gentle. therefore, the following

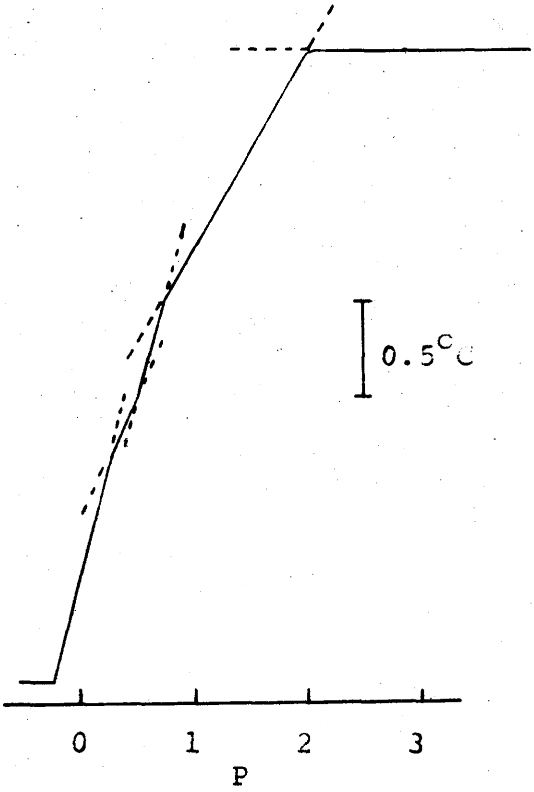


Fig. 1 Thermometric titration of 1.712 x 10^{-1}M Na_2MoO_4 and HCl of 2.232 times the molarity of the molybdate with sodium hydroxide.

reaction can supposed to occur:

$7HMo_8O_{26}^{3-} + 11\ OH^- = 8H_2Mo_7O_{24}^{4-} + H_2O$ ——(VI)

The slope of the curve between p=0.571 and P=0.857 is steeper than that between P=0 and P=0.375, therefore, the following reaction is thought to occur:

$H_2Mo_7O_{24}^{4-} + 2\ OH^- = Mo_7O_{24}^{6-} + 2H_2O$ ———(VII)

The curve from P=0.857 to P=2.00 may correspond to the decomposition reaction of heptamolybdate into monomolybdate.

$Mo_7O_{24}^{6-} + 8\ OH^- = 7MoO_4^{2-} + 4H_2O$ ———(VIII)

In the consequence of the analysis of the back titration the process from $H_2Mo_7O_{24}^{4-}$ to octamolybdate that could not be clarified in the polymerization process, has become apparent. If the same process could be taken reversibly, both in the polymerization can be written by the following equations.

$8H_2Mo_7O_{24}^{4-} + 11H^+ = 7HMo_8O_{26}^{3-} + 10H_2O$ ———(IX)

$HMo_8O_{26}^{3-} + 3H^+ = H_4Mo_8O_{26}$ ————————(X)

Salt effect on polymerization process

The titrations of sodium molybdate solution with hydrochloric acid was also performed in the presence of other neutral salt in the solution. The effect of sodium chloride and of potassium chloride on the titration curve of a definite amount of sodium molybdate are in Tables 2 and 3, respectively, in which Z-value of every inflection point is listed with the varying concentrations of the salt. On the other hand, in Tables 4,5, and 6, these salt effect are shown under the condition a fixed amount of sodium chloride, potassium chloride, and sodium perchlorate, respectively, and varying amounts of sodium molybdate.

Table 2 Results of thermometric titration of 0.06730M sodium molybdate with hydrochloric acid in various concentrations of sodium chloride.

Concentration of NaCl(M)	Z-value* 1st inflection	2nd inflection	3rd inflection
3.0	1.14_3(0.8)**	1.42_6(0.8)**	2.1(1.0)**
2.0	1.14_3(0.8)	1.42_7(0.8)	2.1(1.0)
1.2	1.15_0(0.8)	1.42_0(0.8)	2.3(1.4)
0.6	1.16_9(0.9)	1.41_6(0.8)	2.3(1.9)
0.3	1.17_0(1.0)	1.41_5(0.9)	2.5(2.3)
0.08	1.19_0(1.1)	1.41_0(1.1)	2.6(2.5)
0.04	1.21_3(1.2)	1.41_2(1.1)	2.7(2.5)

* Each Z-value is the average of 10 runs.

** C.V.(%).

Table 3 Results of thermometric titration of 0.06730M sodium molybdate with hydrochloric acid in various concentrations of potassium chloride.

Concentration of KCl(M)	Z-value* inflections 1st	2nd	3rd	4th
3.0	1.14_3(0.8)**	3.00_0(4.4)**	3.8(3.8)**	4.3(10.8)**
2.0	1.14_3(0.8)	2.26_0(4.0)	3.0(3.5)	3.8(10.0)
1.5	1.14_3(0.8)	2.00_4(3.7)	2.2(3.5)	3.8(10.0)
1.0	1.14_3(0.8)	1.87_5(2.4)	2.1(3.4)	3.6(10.0)
0.5	1.14_4(0.8)	1.77_7(2.4)	2.0(3.8)	3.5(11.6)
0.1	1.17_8(1.2)	1.48_9(2.0)	3.2(3.0)	———
0.05	1.19_9(1.2)	1.43_8(1.5)	3.1(2.8)	———

* and ** are similar to in Table 2.

Table 4 Results of thermometric titration of sodium molybdate at various concentrations with hydrochloric acid in the presence of 2.0M sodium chloride.

Concentration	Z-value*		
of Mo(M)	1st inflection	2nd inflection	3rd inflection
$2.140\mathrm{x}10^{-1}$	1.14_3(0.8)**	1.42_9(0.8)**	2.00_9(0.8)**
$1.070\mathrm{x}10^{-1}$	1.14_3(0.8)	1.42_9(0.8)	2.01_3(0.8)
$5.350\mathrm{x}10^{-2}$	1.14_3(0.8)	1.43_0(0.8)	2.2 (1.1)
$2.654\mathrm{x}10^{-2}$	1.14_4(0.9)	1.43_0(1.0)	2.2 (1.6)
$1.070\mathrm{x}10^{-2}$	1.14_2(0.9)	1.43_0(1.0)	2.7 (2.0)
$5.350\mathrm{x}10^{-3}$	1.14_2(1.0)	1.43_0(1.2)	———

* and ** are similar to in Table 2.

Table 5 Results of thermometric titration of sodium molybdate at various concentrations with hydrochloric acid in the presence of 2.0M potassium chloride.

Concentration	Z-value*			
		Inflections		
of Mo(M)	1st	2nd	3rd	4th
$2.140\mathrm{x}10^{-1}$	1.14_3(0.8)**	1.88_8(3.2)**	2.00_9(2.1)**	2.2(5.0)**
$1.070\mathrm{x}10^{-1}$	1.14_2(0.8)	2.00_0(3.5)	2.8 (3.3)	3.5(8.3)
$5.350\mathrm{x}10^{-2}$	1.14_3(0.8)	2.37_4(4.1)	3.0 (3.5)	3.8(10.0)
$2.654\mathrm{x}10^{-2}$	1.14_3(0.8)	2.76_1(4.2)	3.6 (4.0)	———
$1.070\mathrm{x}10^{-2}$	1.14_3(0.9)	3.10_0(4.8)	———	———
$5.350\mathrm{x}10^{-3}$	1.14_3(0.9)	3.8 (8.0)	———	———

* and ** are similar to in Table 2.

Table 6 Results of thermometric titration of sodium molybdate at various concentrations with hydrochloric acid in the presence of 3.0M sodium perchlorate.

Concentration of Mo(m)	Z-value		
	1st inflection	2nd inflection	3rd inflection
$2.140\text{x}10^{-1}$	1.14_3(0.8)**	1.42_8(0.8)**	2.00_0(0.8)**
$1.070\text{x}10^{-1}$	1.14_3(0.8)	1.42_9(0.8)	2.00_9(0.8)
$5.350\text{x}10^{-2}$	1.14_3(0.8)	1.42_7(0.8)	2.2 (1.6)
$1.070\text{x}10^{-2}$	1.14_3(0.9)	1.43_0(0.9)	2.7 (1.9)
$5.350\text{x}10^{-2}$	1.14_3(0.9)	1.43_0(1.0)	————

* and ** are similar to in Table 2.

As can be seen from Tables 2 to 6, the first product in the titration of molybdate solution with hydrochloric acid in the presence of some neutral salt in the solution is the heptamolybdate over the entire range of the concentration of molybdate. The delay of the third inflection which can be seen in Table 3 suggests that the protonated heptamolybdate is apt to bind with its counter-ion. The fourth inflections appearing in Tables 3 and 5 are due to the formation of precipitate, presumablly of potassium octamolybdate. In the presence of large amounts of cations, they might affect on the structure of the hydrate or protonated polymolybdate or hinder the formation of the octamolybdate.

On the other hand, Haeringer *et al.*[33] described from their results of potentiometric measurements in 3M to 0.1M sodium chloride solutions that in higher ionic strength the first-product is heptamolybdate and in lower ionic strength it is hexamolybdate($Mo_6O_{20}^{4-}$). I could not obtained an evidence of the formation of heptamolybdate in low ionic strength solution.

Heats of reaction

The heat of reaction of the polymerization process was estimated from the data of the following thermometric titration curves of sodium molybdate in various concentrations; in 3M sodium perchlorate solution with perchloric acid; in 2M sodium chloride solution with hydrochloric acid. The titration of an acidified solution of molybdate in 1M lithium chloride solution was also carried out with sodium hydroxide. The values of the heats of reaction obtained by the present author are listed in Table 7 together with the values by Arnek *et al.*[37]

Arnek *et al.*[37] had already tried the enthalpy titration of sodium molybdate in 3M sodium perchlorate solution with perchloric acid, and they determined the heat of reaction after treating the data with a computer. The present author obtained directly from the titration curves; however, all of them almost consist with each other except for the following point. For reaction iii in Table 7, Arnek *et al* reported the heat of reaction in the formation of $H_3Mo_7O_{24}^{3-}$ in accordance with their enthalpy titration and the potentiometric titration by Sasaki *et al*.[31]. The present author could not find any exothermic curvature or deflection of the titration curve which shows the formation of $H_3Mo_7O_{24}^{3-}$ after the reaction ii in Table 7 had ceased, but could find the exothermic part of the titration curve which shows the formation of octamolybdate.

Table 7 The heats of reaction for the polymerization of molybdate and for the depolymerization of polymolybdate at 25°C.

Reaction	Medium	ΔH (Kcal/mole)
i) $7MoO_4^{2-} + 8H^+ = Mo_7O_{24}^{6-} + 4H_2O$	3M $NaClO_4$	-55.1
	"	-56.0*
	2M NaCl	-56.7
ii) $Mo_7O_{24}^{6-} + 2H^+ = H_2Mo_7O_{24}^{4-}$	3M $NaClO_4$	+4.0
	"	+3.4*
iii) $H_2Mo_7O_{24}^{4-} + H^+ = H_3Mo_7O_{24}^{3-}$	"	-0.6*
iv) $8H_2Mo_7O_{24}^{4-} + 32H^+ = 7H_4Mo_8O_{26} + 10H_2O$	"	-98.8
v) $H_4Mo_8O_{26} + 3\ OH^- = HMo_8O_{26}^{3-} + 3H_2O$	1M LiCl	-39.3
vi) $7HMo_8O_{26}^{3-} + 11\ OH^- = 8H_2Mo_7O_{24}^{4-} + H_2O$	"	-123.2
vii) $H_2Mo_7O_{24}^{4-} + 2\ OH^- = Mo_7O_{24}^{6-} + 2H_2O$	"	-27.8
viii) $Mo_7O_{24}^{6-} + 8\ OH = 7MoO_4^{2-} + 4H_2O$	"	-55.1

* Arnek *et al*.[37].

From the above results it can be concluded that the predominant species produced in the polymerization process differs from one another depending on the experimental condition such as the amount of salt(ionic strength), the kind of salt, and the concentration of the initial molybdate solution. A considerable confusion of many years to define the predominant species in each case has been brought probably by the dependence of the reaction process on the experimental condition.

TITRATION OF MOLYBDIC ACID WITH SODIUM HYDROXIDE SOLUTION

Summary

To define the properties of molybdenum-containing species which appear in the acidification of neutral molybdate solution with mineral acid, the reverse process, the titration of molybdic acid or acidified molybdate solution with sodium hydroxide, was examined and the titration curves were obtained thermometrically as well as potentiometrically. The thermometric titration curves had their inflections which are not perceptible on the pH-titration curves of the same systems. Titration curves of both methods depended upon the concentration of molybdenum and the reaction process was found to be responsible for this variation of the curve. With the aid of the ultraviolet spectrophotometry of Pungor et al., polymolybdate anions were identified, and a neutral salt such as sodium perchlorate or lithium perchlorate was found to affect on the shape of the thermometric titration curve, since in the presence of such salt octamolybdate ion was readily converted into heptamolybdate ion.

Introduction

In the previous paper I reported an investigation on the formation of molybdenum-containing polyanions in the process of acidification of neutral molybdate solution[38]. That investigation was performed by means of the thermometric titration and the inflections on the titration curves many informations could be introduced. However, the reverse reaction, neutralization of molybdic acid or acidified molybdate solution with alkali hydroxide, was of interest in connection with the above process, and I attempted to carry out the thermometric titration with a titrator of a new type which has been described previously[35] .

The reaction between molybdic acid and alkali hydroxide has been investigated mainly by the pH-titration and by the conductometric titration. Cannon[1] reported two inflections at 0.5 and 2.0 of P-value, the alkali/Mo equivalent ratio, on the pH-titration curve of 0.310M molybdic acid solution prepared by Auger's method[39]. He described also that in the presence of 3M sodium chloride the first inflection shifted to larger P-value while the second remained as it was. This shift was accounted for by the variation of the activity coefficient of hydrogen ion in the solution containing sodium chloride.

Richardson[40] tried the pH- and the conductometric titration with 2.2 x 10^{-4}M molybdic acid prepared by the ion-exchange technique, and reported two inflections on the titration curve at 0.5 and 2.0 of P-value. He observed the titration curves displayed their different forms depending upon the concentration of molybdic acid solution tested. Jain and Jain[41] carried out the pH-titration with 0.018M molybdic acid prepared by the ion-exchange and also found two inflections on the titration curve at 0.5 and 2.0 of P-value; in the presence of 4M sodium chloride, the first shifted to 0.85 while the second still remained at 2.0. These results led the investigators to a conclusion that octamolybdate($Mo_8O_{26}^{4-}$) existed in the initial molybdic acid solution and this was transformable into heptamolybdate($Mo_7O_{24}^{6-}$) in a medium with high ionic strength.

Nevertheless, as has been reported previously I observed four distinct inflections on the thermometric titration curve when acidified molybdate solution in the concentration of molybdenum between 2.29 x 10^{-1} and 1.07 x 10^{-1}M was titrated with sodium hydroxide solution, and the heat of the reaction of the above four steps was estimated from each titration curve[38]. Richardson[40], and Heitner-Wirguin et al[42] concluded that the similar equilibrium could be applied for acidified molybdate solution and for molybdic acid solution as results of the pH- and the conductometric titration[40], and of the ion-exchange technique[42]. The detailed examination of these ionic equilibria was carried out by the thermometric titrations of acidified molybdate solution and molybdic acid solution with wide range of their concentrations and the shape of titration curve was compared with each other and also with the curve obtained by the potentiometric titration. A neutral salt such as sodium perchlorate or lithium perchlorate when existing in the solution, has serious influences on the shape of the titration curve; therefore, these effect were also examined.

Experimental

Reagents

*Molybdic acid solution:** *Twenty grams of sodium molybdate dihydrate of the reagent grade was dissolved in 200ml of distilled water, and the solution was passed through a column of polystylene cation-exchange resin(trade name: Amberleite IR-120, mesh 32 - 100) in the hydrogen form. In order to remove sodium ion completely, the effluent was poured on another column of the same cation-exchanger and this process was repeated till any sodium ion could not be found in the last effluent. After that, 0.2M molybdic acid* solution was prepared by adjusting the volume of the solution to a definite volume. The standardization of the molybdenum content was made gravimetrically after precipitating molybdic acid as its 8-hydroxyquinolinate as usual[13].

* Previously Sasaki et al.[31] prepared about 1M molybdic acid solution by the use of cation exchanger(Dowex 50 X-8) and the solution thus prepared was found to show strong Tyndall effect. After a few days standing white precipitate appeared. However, about 0.2M molybdic acid solution prepared by me was very stable as its Tyndall effect could be observed eventually after ten days and none of the precipitate did appear after one month. I prepared a fresh solution of molybdic acid every three days and the octamer was difined as the predominant species in the solution by the differential spectrophotometric method of Pungor et al.[5].

Preparation of ion-exchanger column. In the above procedure if the cation exchanger contained a reducing material, the resin had to be made free from such impurity. A hundred milliliters of powdered resin was first suspended in acetone for about three hours to remove acetone-soluble materials. Then, the material was poured into distilled water to settle the resin particles and washed with water repeatedly by decantation. Furthermore, the washed resin particles were put into 0.2% potassium dichromate solution and allowed to stand for a day. A slurry of the resin was poured into a glass tube for chromatographic use 1.5 x 60cm, fitted with a sintered glass filter at one end, and the column was prepared. Through this column, 500ml of 3M hydrochloric acid and successively 200ml of 2M sodium chloride solution were passed. Then, 200ml of 3M hydrochloric acid was passed again to make the hydrogen form of resin. Finally the column was washed by passing distilled water sufficiently to remove chloride ion perfectly from the resin.

Acidified molybdate solution. A sodium molybdate solution was made acidic by adding perchloric acid of 2.00 times the molarity of the molybdate. The concentration of molybdenum was determined gravimetrically in a simillar manner as above[13].

All other reagents used in this investigation were of the guranteed reagent grade of Wako Chemicals Co., unless otherwise stated, and without further purification.

Apparatus

Thermometric titrator A thermometric titrator made by TOA Electric Co., was used. Its detailed construction has been described in the previous paper of the present author [35].

All pH mesurements were made using a METROHM potentiograph E 336 with a glass-calomel electrode system calibrated with buffer solutions complying with accepted standards.

All spectrophotometric mesurements were carried out by an automatic SHIMADZU ultraviolet spectrophotometer. Sillica microcuvettes of path length 1.0 - 0.02mm were used.

Procedure

The procedure of the thermometric and pH-titration were just *the same as had been described in the previous papers*[35,38]. *In these cases titrations were carried out for molybdic acid in the concentration range 0.2 - 0.004M. As being described by Richardson*[40], *in every case, the molybdic acid solution was left aside for about twelve hours after its preparation to maintain the homogeneity of the solution. Titrations with sodium hydroxide were performed under the condition that the volume of the titration to be required was not exceeded to 10% of the total volume of the final solution in the titration cell.*

The spectra of the solutions examined were measured against distilled water and neutral monomeric molybdate solution similarly to the method by Pungor et al.[5].

All experiments were conducted at 25°C.

Results and discussion

Thermometric titration curves of molybdic acid and acidified molybdate solution with sodium hydroxide.

The titration curves of molybdic acid in 2.29×10^{-1} M and 4.58×10^{-3}M are shown in Fig. 1 and Fig.2, respectively. In the former four inflections can be observed on the titration curve and in the latter only two inflections. The P-values are listed in Table 1. On the other hand, in consequence of the titration of acidified molybdate solution in 2.14×10^{-1} to 5.35×10^{-3}M with sodium hydroxide solution, the similar titration curves

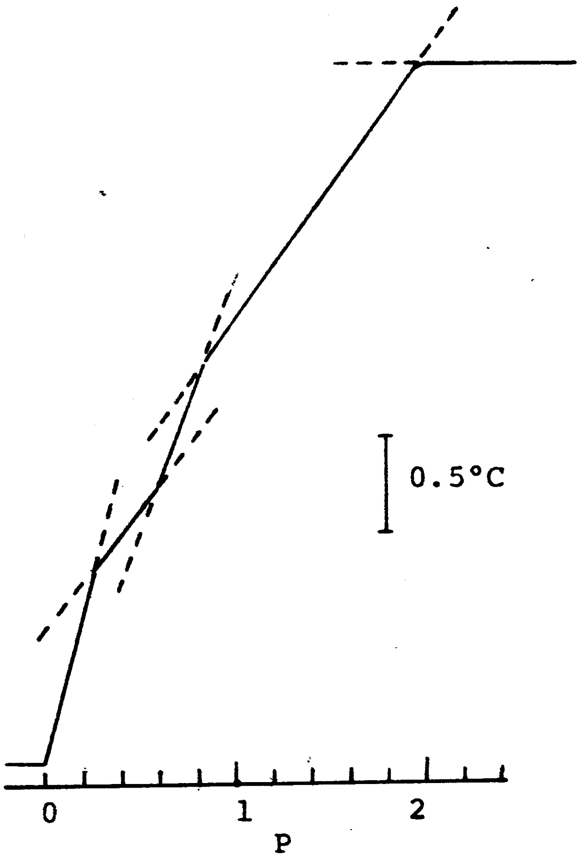


Fig.1 Thermometric titration of 2.29×10^{-1}M molybdic acid with sodium hydroxide. P = number of moles of base added per mole of molybdenum and the ordinate is relative heat change during the titration.

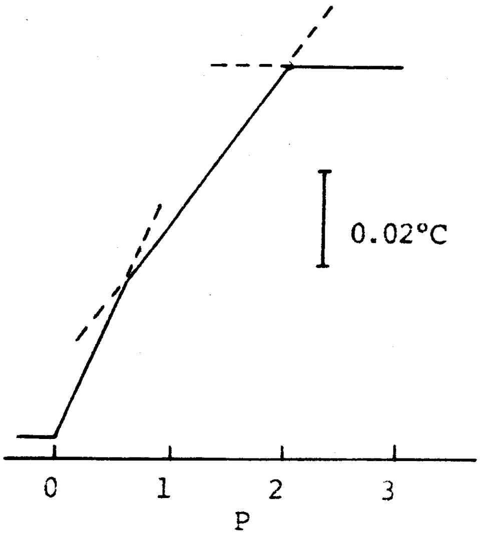


Fig.2 Thermometric titration of 4.58×10^{-3}M molybdic acid with sodium hydroxide.

Table 1 Results of thermometric titration of molybdic acid in various concentractions with sodium hydroxide.

Molybdic acid taken (M)	P-value* inflections 1st	2nd	3rd	4th
2.29×10^{-1}	0.375	0.571	0.857	2.00
1.14×10^{-1}	0.315	0.519	0.722	2.00
9.16×10^{-2}	0.264	0.400	0.687	2.00
6.87×10^{-2}	——	0.312	0.664	2.00
4.58×10^{-2}	——	0.304	0.658	2.00
2.29×10^{-2}	——	——	0.558	2.00
1.14×10^{-2}	——	——	0.511	2.00
9.16×10^{-2}	——	——	0.509	2.00
6.87×10^{-2}	——	——	0.503	2.00
4.58×10^{-3}	——	——	0.501	2.00

* P-value = number of moles of base added per mole of molybdenum.

Table 2 Results of thermometric titration of acidified molybdate solution* in various concentrations with sodium hydroxide.

Molybdate taken (M)	P-value inflections			
	1st	2nd	3rd	4th
2.14×10^{-1}	0.375	0.571	0.857	2.00
1.50×10^{-1}	0.375	0.570	0.857	2.00
1.07×10^{-1}	0.373	0.570	0.857	2.00
8.56×10^{-2}	0.366	0.549	0.850	2.00
6.56×10^{-2}	0.305	0.500	0.827	2.00
4.28×10^{-2}	——	0.463	0.689	2.00
1.07×10^{-2}	——	0.311	0.543	2.00
8.56×10^{-3}	——	——	0.527	2.00
5.35×10^{-3}	——	——	0.508	2.00

* The ratio of acid added to molybdate in an acidified molybdate solution is 2.00.

as in the case of molybdic acid were obtained. The P-values of each titration curves are listed in Table 2. From these data, it is evident that the shape of the titration curve is depending upon the concentration of molybdenum taken initially. The variation of P-value could be observed in a wide range of concentration of molybdic acid rather than that of acidified molybdate. This fact be may be attributed to the variation of ionic strength during the titrations of molybdic acid solution, since in the latter case sodium ion is present in the solution initially and the change of ionic strength is relatively small. Therefore, the shape of the titration curve seems to be determined not only by the concentration of molybdic acid taken initially but by the variation of the ionic strength in the solution during titration.

pH-titrations of molybdic acid and acidified molybdate solution with sodium hydroxide.

The pH-titrations of molybdic acid in 2.10 x $10^{-1}$to 4.20 x 10^{-3}M were carried out. Two inflections appeared on all titration curves. The P-values of the inflections, which were estimated by secondary differentiation of the curve, are shown in Table 3. In the pH-titration of acidified molybdate solution in 2.14 x 10^{-1} to 5.35 x 10^{-3}M with sodium hydroxide, the titration curves of similar type were obtained also. In Table 4, the P-values of the inflections are listed all together.

From these data, the P-value of the second inflection was held constant at about 2.0, while that of the first inflection was 0.6 in higher and 0.5 in lower concentration of molybdic acid. Previous data given by other investigator[1] showed the first inflection was not depening on the concentration of molybdic acid and its P-value held constant at 0.5, potentiometrically. However, Heitner-Wirguin and Cohen reported the variations of the

P-values of both the first and the second inflections with the concentration of molybdic acid from their results on the pH-titration of molybdic acid with sodium hydroxide solution[42]. Surveying these results involving mine and others, the discrepancies are quite difficult to interprete because of the lack of the knowlegdes on the chemical species existing in the solution or appearing during the titration. These apparent results need to be investigated further.

Table 3 Results of pH-titration of molybdic acid in various concentrations with sodium hydroxide.

Molybdic acid taken (M)	P-value	
	1st inflection	2nd inflection
$2.10\mathrm{x}10^{-1}$	0.66	2.0
$1.05\mathrm{x}10^{-1}$	0.63	2.0
$9.03\mathrm{x}10^{-2}$	0.63	2.0
$6.45\mathrm{x}10^{-2}$	0.61	2.0
$4.20\mathrm{x}10^{-2}$	0.59	2.0
$1.05\mathrm{x}10^{-2}$	0.52	2.0
$9.03\mathrm{x}10^{-3}$	0.52	2.0
$6.45\mathrm{x}10^{-3}$	0.51	2.0
$4.20\mathrm{x}10^{-3}$	0.50	2.0

Table 4 Results of pH-titration of acidified molybdate solution in various concentrations with sodium hydroxide.

Molybdate taken (M)	P-value	
	1st inflection	2nd inflection
2.14×10^{-1}	0.64	2.0
1.50×10^{-1}	0.63	2.0
1.07×10^{-1}	0.63	2.0
8.56×10^{-2}	0.61	2.0
6.56×10^{-2}	0.60	2.0
4.28×10^{-2}	0.57	2.0
1.07×10^{-2}	0.52	2.0
8.56×10^{-3}	0.52	2.0
5.35×10^{-3}	0.51	2.0

Richardson[40] has point out that the variety of the titration curves might be caused from the hydrolysis of the salt formed in a dilute solution to some extent. He assumed the hydrolysis from the results in his conductometric titration of molybdic acid with sodium hydroxide solution, encountering with the variation of the titration curves in every case. The present author, however, proposed a new assumption different from the Richardson's, since the variation of the titration curves, either of potentiometric and thermometric, depended upon the concentration of molybdic acid or acidified molybdate taken initially and this variation must show the difference of the reaction process in each case.

The chemical species existing in the solution before the titration was identified as octamolybdate ion and that after the titration monomeric molybdate ion by the spectrophotometry[5].

From Tables 1 - 4 and spectrophotometric measurements, I concluded that reaction processes in the titration of about 2 x 10^{-1}M molybdic acid or acidified molybdate solution with sodium hydroxide solution might be consisted of the following four steps:

$H_4Mo_8O_{26} + 3\ OH^- = HMo_8O_{26}^{3-} + 3H_2O$ (P=0 - 0.375) ——(1)

$7HMo_8O_{26}^{3-} + 11\ OH^- = 8H_2Mo_7O_{24}^{4-} + H_2O$ (P=0.375 - 0.571) ———(2)

$H_2Mo_7O_{24}^{4-} + 2\ OH^-\ Mo_7O_{24}^{6-} + 2H_2O$ (P=0.571 - 0.857) —(3)

$Mo_7O_{24}^{6-} + 8\ OH^- = 7MoO_4^{2-} + 4H_2O$ (P=0.857 - 2.00) —— (4)

On the other hand, in the titration of about 5 x 10^{-3}M molybdic acid or acidified molybdate solution P-values of the inflections seem to prove the existence of the following two reaction processes:

$H_4Mo_8O_{26} + 4\ OH^- = Mo_8O_{26}^{6-} + 4H_2O$ (P=0 - 0.500) ——(5)

$Mo_8O_{26}^{4-} + 12\ OH^- = 8MoO_4^{2-} + 6H_2O$ (P=0.500 - 2.00) —(6)

It is supposed that in the range above 4 x 10^{-2}M the reactions 1 - 4 are predominant and reactions 5 and 6 are subdominant, while below that concentration reactions 5 and 6 become predominant and reactions 1 - 4 subdominant.

Titrations of molybdic acid with sodium hydroxide solution in the presence of sodium perchlorate or litjium perchlorate.

Molybdic acid in 2.00×10^{-1} to 2.00×10^{-2}M in 4M sodium perchlorate solution was titrated with sodium hydroxide solution and the thermometric titration curves were obtained; Fig.3 shows that of 2.00×10^{-1}M molybdic acid and Fig. 4 that of 2.00×10^{-2}M molybdic acid, and in Table 5 P-values of the inflections of titration curves for molybdic acid in various concentrations. In the case of 2.00×10^{-1}M molybdic acid, three inflections were observed, and in the case of 2.00×10^{-2}M the P-value of the first inflection was 0.856 wheras in the absence of sodium perchlorate the value of the first inflection was 0.542. The pH-titration curves were also obtained under the same condition for 2.00×10^{-1} to 2.00×10^{-2}M molybdic acid in 4M sodium perchlorate solution. Each titration curve was similar to the corresponding one of the pH-titration curves(not showed in this text), and the P-values of the inflections of the curves are in Table 6. It seems to be important the influence of sodium perchlorate on the P-values of the first inflections in various concentrations of molybdic acid.

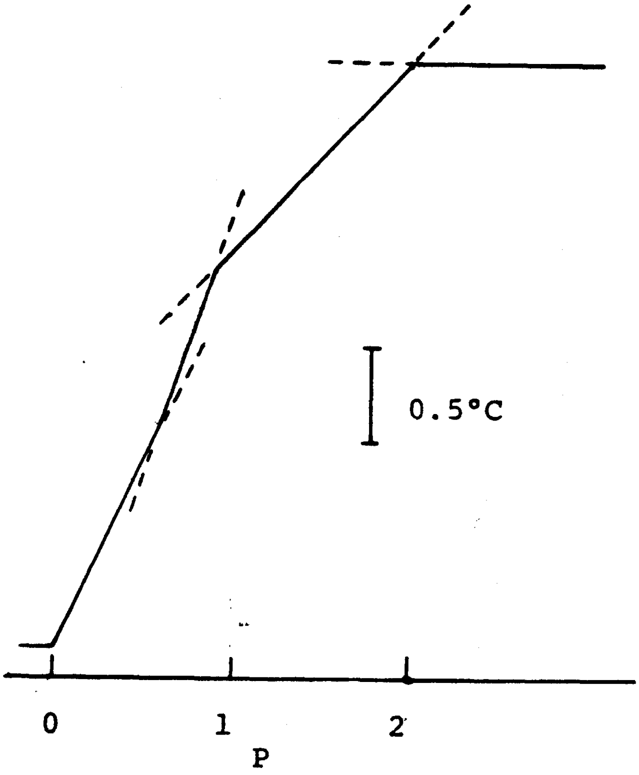
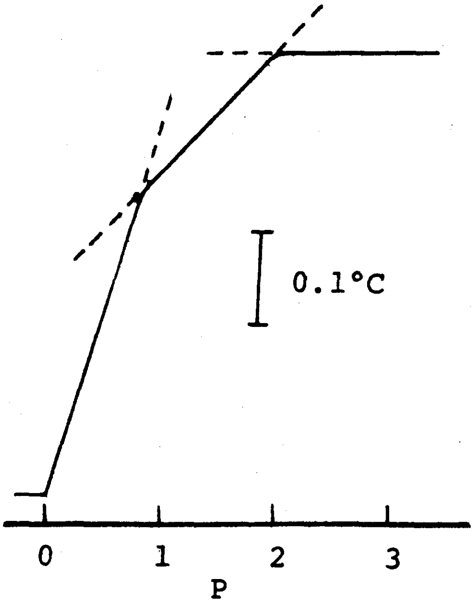


Fig. 3 Thermometric titration of 0.200M molybdic acid with sodium hydroxide in the presence of 4.0M sodium perchlorate.



Eig. 4 Thermometric titration of 0.0200M molybdic acid with sodium hydroxide in the presence of 4.0M sodium perchlorate.

Table 5 Results of thermometric titration of molybdic acid in various concentrations with sodium hydroxide in the presence of 4.0M sodium perchlorate.

Molybdic acid	P-value		
taken (M)	1st inflection	2nd inflection	3rd inflection
2.00×10^{-1}	0.602	0.857	2.00
1.00×10^{-1}	0.670	0.857	2.00
8.00×10^{-2}	0.735	0.857	2.00
6.00×10^{-2}	0.814	0.858	2.00
4.00×10^{-2}	0.835	0.857	2.00
2.00×10^{-2}	——	0.856	2.00

Table 6 Results of pH-titration of molybdic acid in various concentrations with sodium hydroxide in the presence of 4.0M sodium perchlorate.

Molybdic acid	P-value	
(M)	1st inflection	2nd inflection
2.00×10^{-1}	0.81	2.0
1.00×10^{-1}	0.82	2.0
8.00×10^{-2}	0.82	2.0
6.00×10^{-2}	0.82	2.0
4.00×10^{-2}	0.84	2.0
2.00×10^{-2}	0.84	2.0

I examined exclusively the first inflection of the thermometric titration curves for 2.00 x 10^{-2}M molybdic acid in the presence of the perchlorate in varying concentrations, and the results are shown in Table 7. In these experiments the second inflection remained constant at the P-value of 2.00 in all runs. It can be seen from Table 7 that the amount of the neutral salt necessary to change the P-value of the first inflection from 0.542 to 0.856 differs between sodium salt and lithium salt, *i.e.*, above 3.0M of sodium perchlorate and above 4.4M of lithium perchlorate. The difference of the salt concentration between sodium perchlorate and lithium perchlorate to be required to display the salt-effect sufficiently seems therefore to be in conflict with Cannon's interpretation of the salt-effect, in which he discussed only from the data of the experiments in the presence of sodium chloride. On the other hand, Heitner-Wirguin *et al.*[42] said that this difference might be caused by the extent of protonation of molybdate owing to the difference in hydration of cations and anions of the salt added. Leaving these assumptions out of the account, the present author measured the absorption of 2.00 x 10^{-2}M molybdic acid in 4M sodium perchlorate solution against sodium monomeric molybdate in the region 210 to 330mμ[5] and obtained the spectrum with only a well defined maximum at 258mμ. The molybdenum-containing species in this solution was revealed as being heptamolybdate ion and not octamolybdate ion. This fact shows the validity of the assumption on the salt-effect described by Jain and Jain[41]. Therefore, I concluded that the reactions proceeding in the titration of 2.00 x 10^{-2}M molybdic acid in 3M sodium perchlorate or in 4.4M lithium perchlorate with sodium hydroxide solution might be consisted of the following two steps:

$H_6Mo_7O_{24} + 6\ OH^- = Mo_7O_{24}^{6-} + 6H_2O$ (P=0 - 0.857)

$Mo_7O_{24}^{6-} + 8\ OH^- = 7MoO_4^{2-} + 4H_2O$ (P=0.857 - 2.00).

Table 7 Salt-effect of sodium perchlorate and lithium perchlorate on P-value of the first inflection of the thermometric titration curve; molybdic acid: 2.00x10^{-2}M.

Perchlorate taken(M)		P-value of the first inflection
none		0.542
$NaClO_4$	2.0	0.843
	2.5	0.850
	3.0	0.858
	3.5	0.857
	4.0	0.858
$LiClO_4$	3.3	0.788
	3.9	0.831
	4.4	0.857
	5.0	0.857

EFFECTS OF SALTS ON THE POLYMERIZATION OF MOLYBDATE AND THE DEPOLYMERIZATION OF MOLYBDIC ACID.

Summary

The polymerization process of molybdate and the depolymerization process of molybdic acid were investigated in the presence of various salts by the thermometric titration. The inflection points of the titration curves could interpret the mechanism of the process, since Z-value(H^+/Mo*) and P-value(*OH^-/Mo*) of the inflection point vary with the amount of a salt as well as with the kind of the salt. The salt-effect displays in the increasing order as follows:* $LiCl < NaCl < MgCl_2 < NH_4Cl < KCl < RbCl < CsCl$. *A linear relationship was found to exist between the amount of a salt necessary to reveal the salt-effect completely and the reciprocal of the Stokes' radius of the cation of salt present in the polymerization of molybdate and in the depolymerization of molybdic acid. The salt-effect was considered to be based on the formation of an ion-pair between heptamolybdate and a cation in question.*

Introduction

Many investigators carried out to study the salt-effect of sodium chloride alone on the polymerization process[1,33] or on the depolymerization process[41] by the pH-titration. Heitner-Wirguin and Cohen[42] had investigated the salt-effect on the formation of polymolybdate species with the aid of the ion-exchange and the spectrophotometry, and they concluded that the extent of the salt-effect of cations decreased in the order, potassium chloride > ammonium chloride > sodium chloride > lithium chloride > magnesium chloride and that these differences of the effects might be attributed to the degree of hydration of cations and anions of the salt present.

By the thermometric titration the present author investigated in some detail the salt-effect, and the decreasing order of the effect was recognized for a series of alkali metal salts, and the effect was discussed on the basis of above order and the radii of hydrated cations, with an aid of spectrophotometry as a means of identification of molybdate species occuring in the each process.

Experimental

Reagents

Lithium molybdate solution. *Lithium molybdate dihydrate of the reagent grade was dissolved in water to make its 0.5M solution, and this solution was diluted to an appropriate concentration. The concentration was determined gravimetrically by weighing precipitate of molybdenum 8-hydroxyquinolinate as usual*[13]. *The* *content of the cationic species was checked by passing the solution through a column of Amberlite ITA-401 in hydroxide form and by titrating the effluent with a standard solution of hydrochloric acid.*

Dilute hydrochloric acid. The 35% reagent grade hydrochloric acid was diluted with water to an appropriate concentration. The solution was standarized with a standard sodium carbonate solution as usual.

Molybdic acid solution. A 0.2M molybdic acid solution was prepared by cation exchange from lithium molybdate solution with a column of Amberlite IR-120 in the H^+ form. The standarization of the molybdenum content was made gravimetrically after precipitating molybdic acid as its 8-hydroxyquinolinate[13]. The solution was diluted to an appropriate concentration. The details of preparation and stability of molybdic acid solution has been described before[43].

Sodium hydroxide solution. Sodium hydroxide of the reagent grade was dissolved in degassed water to make an appropriate concentration solution. The solution was titrated with a standard hydrochloric acid solution as usual.

Other reagents such as lithium chloride, sodium chloride, potassium chloride, rubidium chloride, cesium chloride, magnesium chloride, and ammonium chloride were all of the reagent grade, and these were used without further purification.

Apparatus

A thermometric titrator of new type having two injection syringe type automatic burettes and two titration cells was used. Its detailed construction has been described in the previous paper[35]. All spectrophotometric measurements were carried out by an automatic Shimadzu ultraviolet spectrophotometer. The measurments were made in the region from 212 - 333nm. The spectra of the solution examined were measured against neutral monometric molybdate solution using 10mm or 1.0mm path length sillica cuvette. The octamolybdate and heptamolybdate were identified by these difference spectra in a similar manner as Pungor et al[5].

Procedure

The procedure of the thermometric titration were just same as had been described in the previous papers[38,43]. The titration cell(Dewar flask) contained 20ml of lithium molybdate solution or molybdic acid solution, with varying amounts of chloride. The titration rate was 1ml in 12min. The concentration of titrant was kept to be about 100 times that of the titrand. A thermogram was about 1000mm long for each titration. All titrations were carried out at a nominal temperature of 25°C in a constant temperature room, after the solutions had achieved thermal equilibrium with their surroundings.

Results

Effects of salts on the polymerization process of molybdate.

Varing amounts of each, lithium chloride, sodium chloride, potassium chloride, rubidium chloride, cesium chloride, ammonium chloride and magnesium chloride were added respectively in a 0.08M lithium molybdate solution and the solution was titrated with hydrochloric acid. The titration curves were identical with those in shape appeared in Ref.35, the figures, therefore, being omitted in this paper, and the Z-values , molar ratio of hydrochloric acid added to molybdate at the inflection, of the first and the second inflections in the titration curves are shown Table 1. As the first inflection is in response to the formation of heptamolybdate, when Z-value becomes up to 1.14_3(8/7), the effect of the salts seems to become fully effective[38]. All the salts differed from one another in the amount of salt to be required to reveal its salt-effect completely. The extent of the salt-effects of cations decreases in the following order; $CsCl > RbCl > KCl > NH_4Cl > MgCl_2 > NaCl > LiCl$. This order differs sufficiently from that of Heitner-Wirguin *et al.*[42], though they did not examine about rubidium and cesium salts.

Table 1 Salt-effects of chlorides on Z-values of the first and the second inflections of the thermometric titration curves. Li_2MoO_4: 0.08035M. Each Z-value is the average of 10 runs. * are C.V.(%).

Chloride taken (M)		Z-value	
		1st inflection	2nd inflection
None		1.21_5(1.0)*	1.41_0(1.0)*
LiCl	2.60	1.14_5(0.9)	1.42_6(0.9)
	2.70	1.14_3(0.8)	1.42_9(0.9)
	2.80	1.14_3(0.8)	1.42_9(0.9)
NaCl	1.90	1.14_5(0.8)	1.42_8(0.9)
	2.00	1.14_3(0.8)	1.43_0(0.9)
	2.10	1.14_3(0.8)	1.43_1(0.9)
$MgCl_2$	1.70	1.14_5(0.8)	1.42_8(0.9)
	1.80	1.14_3(0.8)	1.43_2(0.9)
	1.90	1.14_3(0.8)	1.43_5(0.9)
NH_4Cl	0.40	1.14_7(0.9)	1.47_8(1.0)
	0.43	1.14_5(0.8)	1.49_0(1.0)
	0.45	1.14_3(0.8)	1.50_6(1.1)
KCl	0.37	1.14_7(0.9)	1.56_5(1.5)
	0.38	1.14_3(0.8)	1.57_7(1.8)
	0.39	1.14_3(0.8)	1.57_9(1.8)
RbCl	0.20	1.14_9(0.9)	—
	0.21	1.14_5(0.9)	—
	0.22	1.14_3(0.9)	—
	0.23	1.14_3(0.8)	—
CsCl	0.17	1.14_7(0.9)	—
	0.18	1.14_5(0.9)	—
	0.19	1.14_3(0.8)	—
	0.20	1.14_3(0.8)	—

The second inflection shows the addition of two protons to the heptamolybdate ion, therefore, when its Z-value becomes to 1.42_9(10/7), the reaction can be assumed to have finished completely. However, in the presence of potassium chloride or ammonium chloride in its minute concentration, Z-value was shifted enormously. The magnitude of the shift for each salt can be ordered as follows; $KCl > NH_4Cl > MgCl_2 > NaCl > LiCl$ and in this case, rubidium chloride and cesium chloride form the precipitate with polymolybdate formed after the first inflection, therefore, the second inflection could not be measured because of the interference of the heat of precipitation.

The molybdate solution of 0.06M, 0.04M and 0.02M were also titrated, and the same order was obtained each molybdate solution.

By the spectrophotometric measurements in the ultraviolet region, heptamolybdate between the first and the second inflections and octamolybdate after the second inflection were found to be predominant when the salt-effect displayed completely.

Effect of salts on the depolymerization process of molybdic acid.

Varying amounts of lithium chloride, sodium chloride potassium chloride, ammonium chloride, and magnesium chloride were added respectively in a 0.02M molybdic acid solution and the solution was titrated with sodium hydroxide solution. The titration curves obtained were identical with those appeared in Ref.43 in shape. Rubidium chloride and cesium chloride could not be examined as they formed white precipitate with polymolybdate. The experimental results are summarized in Table 2, in which only P-values, molar ratio of sodium hydroxide added to molybdic acid(mole of molybdenum per liter), at the first inflection are shown and the second inflections are omitted, because the latter always shows a constant P-value of 2.00 in all cases either of the presence of salts or not. As the first inflection on the curve is based on the neutralization of heptamolybdenum molybdic acid $H_6Mo_7O_{24}$[43], when the P-value becomes to 0.857_1(6/7), the salt-effect seems to display completely. All the salts could manifest this effect fully as shown in Table 2 and some differences between individual salts resulted. The extent of the salt-effects of cations decreases in the following order; KCl> NH_4Cl> $MgCl_2$> NaCl> LiCl. This order is identical with that of the polymerization process of molybdate described the preceding section. Consequently, the same mechanism would be assumed for the salt-effects.

Table 2 Salt-effects of chlorides on P-values of the first inflection of the thermometric titration curves. Molybdic acid: 0.02222M. Each P-value is the average of 10 runs. * are C.V.(%).

Chloride taken (M)		P-value of the first inflection
None		0.553_6(1.0)*
LiCl	4.45	0.854_7(0.9)
	4.47	0.856_4(0.8)
	4.48	0.857_1(0.8)
	4.49	0.857_1(0.8)
NaCl	3.07	0.885_2(0.9)
	3.09	0.856_6(0.8)
	3.10	0.857_1(0.8)
	3.12	0.857_1(0.8)
$MgCl_2$	2.96	0.855_3(0.9)
	2.98	0.856_1(0.8)
	3.00	0.857_1(0.8)
	3.02	0.857_1(0.8)
NH_4Cl	0.55	0.853_7(0.9)
	0.57	0.856_3(0.8)
	0.58	0.857_1(0.8)
	0.59	0.857_1(0.8)
KCl	0.49	0.854_6(0.9)
	0.50	0.856_5(0.8)
	0.51	0.857_1(0.8)
	0.52	0.857_1(0.8)

The molybdic acid solutions of 0.01M and 0.008M were also titrated and the same order was obtained.

By the spectrophotometric measurements in the ultraviolet region, heptamolybdate could be found to be predominant in the test solution taken initially when the salt-effects displayed completely.

Discussion

The salt-effects described above seem to be related to the Stokes'radii of the cations participating in the polymerization and depolymerization processes. In the case of 0.08M molybdate solution, when the amount of a salt to be required to reveal its salt-effect completely on the polymerization is plotted as abscissa and the reciprocal of the Stokes'radius of the cation as ordinate, a linear relationship could be obtained after calculated by the method of least-square, being shown as the line A in Fig.1, and being expressible as $Y = -0.176_3X + 0.897_2$ with coefficient of correlation -0.9998_9. In the case of 0.06560M, 0.04560M, and 0.02140M, the lines could be expressed as $Y = -0.213_6X + 0.897_0$ with -0.9997_1, $Y = -0.307_3X + 0.897_1$ with -0.9997_0 and $Y = -0.654_7X + 0.897_3$ with -0.9996_5, respectively.

In the case of 0.02M molybdic acid, the linear relationship could also be obtained, being shown as the line B in Fig.1 and expressible as $Y = -0.101_5X + 0.876_5$

with coefficient of correlation -0.9991_0. In the case of 0.01110M and 0.008115M, the lines could be expressed as $Y= -0.202_4X + 0.876_6$ with -0.9995_8 and $Y= -0.276_8X + 0.876_7$ with -0.9993_7.

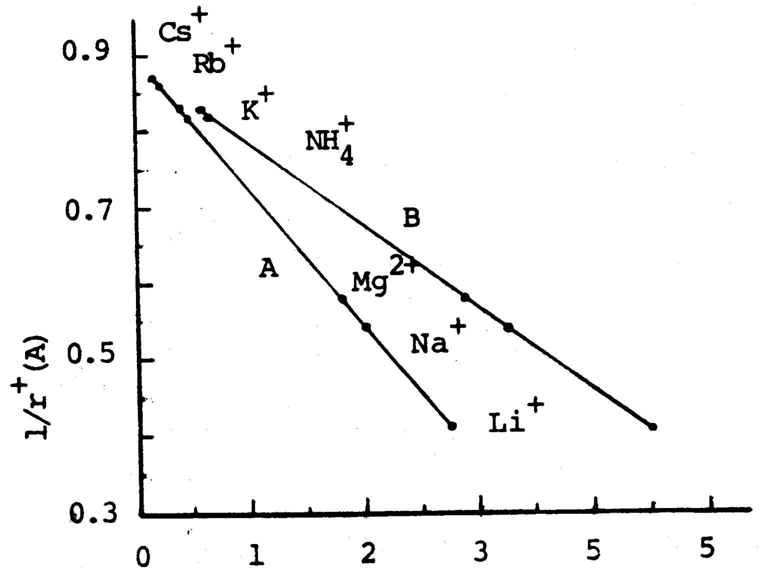


Fig. 1 The linear relationships between the reciprocal of the Stokes'radius of the cation and the amount of a salt to be required to reveal its salt-effect completely, line A: on the polymerization of 0.08035M molybdate, line B: on the depolymerization of 0.02222M molybdic acid. Stokes'radius(r^+) of each cation is Cs^+ 1.155A, Rb^+ 1.16A, K^+ 1.21A, NH_4^+ 1.225A, Na^+ 1.80A, Mg^{2+} 1.725A and Li^+ 2.36A[44].

If the salt-effect displays completely, the reaction series, $MoO_4^{2-} \rightarrow Mo_7O_{24}^{6-} \rightarrow H_2Mo_7O_{24}^{4-} \rightarrow HMo_8O_{26}^{3-}$, proceeds, while when the salt-effect is insufficient another reaction, $Mo_7O_{24}^{6-}$ changes directly into $HMo_8O_{26}^{3-}$ not through by way of $H_2Mo_7O_{24}^{4-}$, proceeds parallel to the above reaction series. These have already been discussed in the preceding paper[38]. The linear relationships were explained on the basis of the formation of the ion-pair between the hydrated cation and $Mo_7O_{24}^{6-}$. Needless to say, $Mo_7O_{24}^{6-}$ is also hydrated. The ion-pair thus formed is also anticipated to hinder the direct conversion, not through $H_2Mo_7O_{24}^{4-}$ into $HMo_8O_{26}^{3-}$. This assumption is supported experimentally by the results of the spectrophotometric measurment.

The magnitude of the shift of the Z-value of the second inflection from the standard value 1.42_9(10/7) shows that a cation of smaller Stokes'radius can combine more strongly with $Mo_7O_{24}^{6-}$ to form an ion-pair, and, therefore, the formation of $H_2Mo_7O_{24}^{4-}$, protonation process, may be hindered. In the case of a larger cation, this effect will be reduced.

In the reverse course, in the neutralization of molybdic acid, a hydrated cation is apt to combine rather strongly with heptamolybdate than octamolybdate, and, consequently, when the salt-effect is reduced, the balance of the following interconversion is displaced remarkably to left hand, while the salt-effect is predominant displaced significantly to right hand.

$$7Mo_8O_{26}^{4-} + 10H_2O = 8Mo_7O_{24}^{6-} + 2OH^+$$

Neverthless, it may be a question that the slopes of the lines at the same concentration of molybdate and molybdic acid(0.02M) differ from each other remarkably, but these will be interpreted as follows. The minimum amount of a salt required to realize its perfect salt-effect on the polymerization process of molybdate is just the amount enough to hinder the conversion of heptamolybdate into octamolybdate temporarily. Namely, protonation of heptamolybdate to $H_2Mo_7O_{24}^{4-}$ should proceed while heptamolybdate is stabilized in the solution by the minimum amount of a salt. On the other hand, in the neutralization of molibdic acid the amount of a salt necessary to shift the above equation so far to the right should be put into the solution. In other words, the straight lines in polymerization show the *dynamic* amount of the salts necessary to shift the above equation to the right and the lines in depolymerization show the *statical* amount of the salts.

Aveston *et al.*[4] described that whether appreciable binding of sodium ion or lithium ion by the polymolybdate occurs is not clear from their results of ultracentrifugation, acidity measurment, and Raman spectroscopic measurments. On the other hand, we could clarify this phenomenon by the results of the thermometric titration with the aid of the u.v. spectrophotometry.

PART III

THERMOMETRIC TITRATION USING DIFFERENTIAL THERMISTOR

THERMOMETRIC TITRATION OF SOME MOLYBDATES, MOLYBDIC ACID, AND MOLYBDENUM TRIOXIDE.

Summary

A thermometric titrator equipped with differential thermistor is used for the titration of molybdenum in sodium molybdate, potassium molybdate, magnesium molybdate, tetramethylammonium molybdate, and tetraethylammonium molybdate, based on their reactions with hydrochloric acid, and in ammonium paramolybdate, molybdic acid, and molybdenum trioxide, based on their reactions with sodium hydroxide. Orthomolybdates and ammonium paramolybdate were determined in the 0.005 - 0.5M range; sufficient solid molybdic acid or molybdenum trioxide was taken to give a final 0.01 - 0.5M solution in 20ml of water. The method is simple and very quick. The standard deviation varies from 0.5 to 1.5% depending on the amount of sample taken.

Introduction

Molybdates, molybdic acid, and molybdenum trioxide of reagent grade are usually assayed gravimetrically as the oxinate complex, $MoO_2(C_9H_6ON)_2$[45-47,13]. Orthomolybdate

(MoO_4^{2-}) is often determined by titrating its neutral solution with a standard lead(II) solution[48,49] or by back-titrating the excess of an added complexone[50,51] Redox titrations can be applied for the determination of molybdenum(VI) after its reduction[52].

Burns *et al.*[53] developed a method of assaying ammonium paramolybdate[$(NH_4)_6Mo_7O_{24}$], in which a sample solution was titrated with a standard sodium hydroxide solution, the change of pH on depolymerization of polymolybdate being followed. However, no method for assaying orthomolybdate based on its polymerization paramolybdate on titration with a mineral acid, seems to have been reported. This is probably because, in all cases of pH titration[1,35] , conductometric titration[11] and thermometric titration[35,43] , the equivalence point (molar ratio of acid added to molybdenum) varied with the concentration of molybdate initially taken; The molar ratio varied from 1.143 to 1.500 at the first inflection of the titration curve. Cannon[1] , investigating the reaction between alkali molybdate and a mineral acid suggested the possibility of a conductometric titration of molybdate at concentrations of 0.007 - 0.07M with an accuracy of 0.3%.

The present author have investigated the same reaction with the aid of thermometric titrations[35,43] ;

it was found that when a neutral salt such as alkali chloride was added to the test solution, the molar ratio at the inflection point no longer varied with the concentration of molybdate, but was constant at 8/7=1.143. The reaction thus proceeded quantitatively as molybdate was titrated with acid:

$7MoO_4^{2-} + 8H^+ = Mo_7O_{24}^{6-} + 4H_2O$

and this was applied for the thermometric titration of molybdates.

In the work described here, the depolymerization of ammonium paramolybdate with sodium hydroxide solution was also applied for the thermometric determination of polymolybdate. As is well known, molybdic acid(MoO_3H_2O) and molybdenum trioxide are only slightly soluble in water; therefore, they were first dissolved in a definite volume of standard sodium hydroxide solution, the excess of which was then back-titrated with standard hydrochloric acid solution. This was recommended by Burns *et al.*[53] for the pH-titration of molybdic acid. However, the thermometric titration is preferable, because the suspension of molybdic acid and molybdenum trioxide does not interfere and the molybdic acid and molybdenum trioxide can be determined directly with sodium hydroxide standard solution.

With regard to the thermometric titration, Jordan[54], Tyrrell and Beezer[55], and Bark and Bark[56] have described the theory and the instrumentation. The thermal change is usually detected by a single thermistor or two thermistors in a bridge, and the end-point of the titration is determined as the point of intersection after extrapolation of the titration curve before and after the end-point; however, the reproducibility is invariably poor when the inflection of the curve is not sharp. Accordingly, the present author employed a differential thermistor probe[57-59] in order to obtain more precise data.

Experimental

Reagents

Orthomolybdates. In order to prepare solution of various molybdates, a specially prepared molybdic acid solution[43] which was 0.1M in molybdenum, was treated with lithium hydroxide, sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide or tetraethylammonium hydroxide in double the molar quantity of molybdic acid was added to prepare magnesium molybdate. These solutions were evaporated to dryness and the powdered molybdates obtained were dried in vacuo at 40°C. The molybdenum content of the molybdic acid and molybdate solutions was determined gravimetrically with oxine[13].

Samples. Sodium molybdate, potassium molybdate, ammonium paramolybdate, molybdic acid(molybdenum trioxide monohydrate), and molybdenum trioxide(guaranteed reagents, Wako Chemicals Co.) were used without purification. Other molybdates were prepared as above. Molybdic acid and molybdenum trioxide were dissolved in sodium hydroxide solution, and molybdenum was determined gravimetrically[13].

Hydrochloric acid solutions. Suitably diluted reagent-grade hydrochloric acid was standardized against sodium carbonate in the usual way.

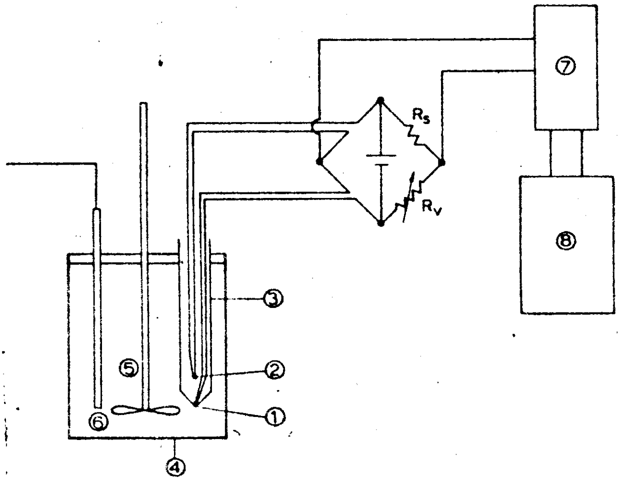
Sodium hydroxide solutions. These were prepared from solid reagent and standardized against hydrochloric acid.

Potassium permanganate solutions. Reagent-grade potassium permanganate was dissolved in water; standardization against sodium oxalate was used.

Other reagents were of reagent grade, and were used without purification.

Apparatus

Thermometric titrator. A thermometric titrator with an electric recorder(TOA Electronics Co.) was employed. The differential thermistor probe consisted of two thermistors of identical temperature characteristics(B-constant 2800±10°K, $R_{25}=20\mathrm{K\Omega}\pm10\%$, time constant 0.3s), connected to a bridge circuit. The two thermistors were placed in a glass probe, as shown in Fig.1 so as to give a time-lag between the responses of the two thermistors. The difference in the responses of the two thermistors was detected, for exothermic or endothermic reactions, thoughout the titration; the output of the probe was connected to the recorder. The end-point of the titration was obtained from the inflection point of the recorded curve of thermal difference against titrant volume.



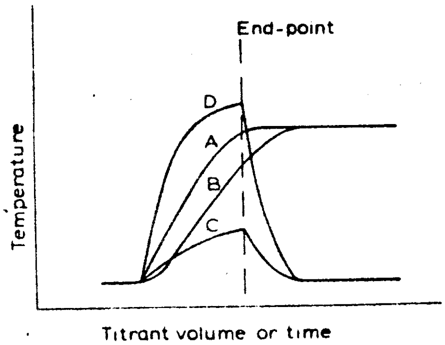


Fig. 1. Thermometric titration apparatus equipped with differential thermostor. (1) Normal response thermistor; (2) delayed-response thermistor; (3) glass probe, o.d. 5 mm; (4) titration cell, 50-ml Daiflon; (5) stirrer; (6) capillary nozzle; (7) amplifier; (8) recorder; Rs = 20 kΩ, Rv = variable resistor.

Fig. 2. Thermometric titration curves. (A) By normal-response thermistor, (B) by delayed-response thermistor alone, (C) by difference in temperature change between (A) and (B), (D) by differential thermistor (amplified C).

For reference, titration curves obtained with the normal response thermistor, the delayed-response thermistor, and the differential thermistor couple are shown in Fig.2; the difference between the two curves obtained with single thermistors(curve C) is amplified when both are used(curve D). In order to check this curve, the titration curves obtained with two injection syringe-type automatic burettes[35] were obtained at the same time as previously described.

Potentiometric titrator. A Metrohm Potentiograph E 336 and glass electrode were used.

Procedure

In the case of molybdates, samples were taken in the following weights so as to give 0.005 - 0.5M solutions in 200ml measuring flasks: sodium molybdate, 0.242 - 24.2g; potassium molybdate 0.328 - 32.8g; magnesium molybdate, 0.202 - 20.2g; tetramethylammonium molybdate 0.326 - 32.6g; tetraethylammonium 0.438 - 43.8g; ammonium paramolybdate 0.173 - 17.3g. The weighed sample was dissolved in water together with 7.5g of potassium chloride, and the solution was transferred to a 200ml measuring flask and diluted with water to the mark. A 20ml aliquot of this solution was pipetted into a 50ml titration cell made of Daiflon(a trifluorochloroethylene polymer) and titrated with a standard solution of hydrochloric acid. In the case of ammonium paramolybdate, potassium chloride was added, and the solution was titrated with a sodium hydroxide solution.

In the case of molybdenum trioxide or molybdic acid, the weights were selected to give a 0.01 - 0.5M solution in a 50ml titration cell: molybdic acid, 0.033 - 1.6g; molybdenum trioxide, 0.029 - 1.4g. Water(20ml) was added and the solution was titrated with a standard sodium hydroxide solution.

The concentration of the titrant was chosen so that the volume required at the end-point would not exceed 10% of the titrand volume. The titrant was injected at a rate of 2ml per

5min from an automatic syringe burette with a capillary nozzle. The titration curve was recorded at a constant chart speed of 12cm min^{-1}.

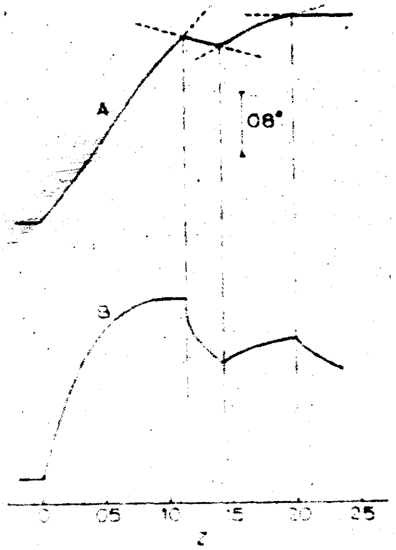
Results and discussion

Titration curves

Titration curves for 0.4M lithium molybdate with hydrochloric acid(Fig.3), 0.01M ammonium paramolybdate with sodium hydroxide solution(Fig.4), and 0.1M molybdenum trioxide with sodium hydroxide solution(Fig.5) are given to illustrate the results obtainable; curves obtained by a reference method are also shown. It can be seen that the titration curves by the differential method give much sharper inflections than those by the reference method, so that end-points can be detected more readily.

Titration of orthomolybdate

In the titration of orthomolybdate with an acid, the Z-value of the first inflection of the curve varies from 1.143(the normal value) when the concentration of molybdate is less than 0.09M: the Z-value becomes 1.500 when the concentration is as low as 0.005M. However, when a neutral salt such as potassium chloride is added, the Z-value is fixed at 1.143 in every case. This salt effect of chlorides has been shown to decrease in the following order: Cs> Rb> K> NH_4> Na> Mg> Li.[61]



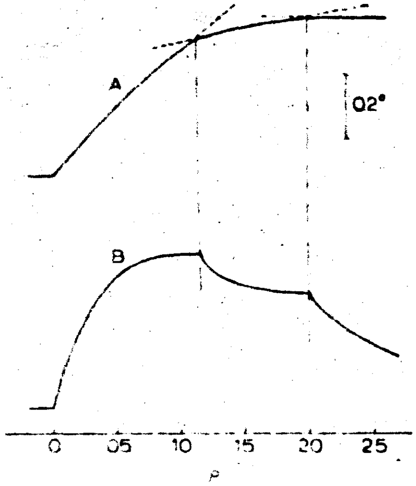


Fig. 3. Thermometric titration of 0.4100 *M* lithium molybdate with hydrochloric acid. The ordinate is the relative heat change during the titration; *Z* is the number of moles of acid added per mole of molybdate. (A) By reference method, and (B) by differential method.

Fig. 4. Thermometric titration of 0.01132 *M* ammonium paramolybdate with sodium hydroxide. *P* is the number of moles of base added per mole of molybdenum. (A) By reference method, and (B) by differential method.

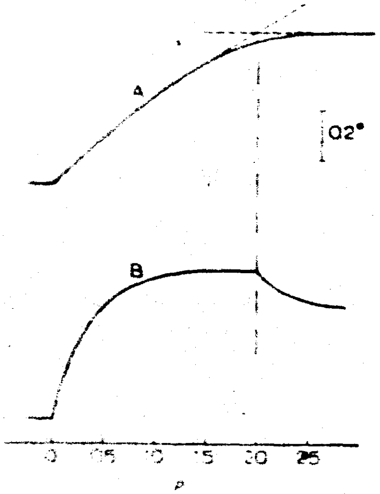


Fig. 5. Thermometric titration of 0.002013 mole of MoO_3 in 20 ml of water with sodium hydroxide. *P* is the number of moles of base added per mole of molybdenum trioxide. (A) By reference method, and (B) by differential method.

Potassium chloride was preferred for its effectiveness and cost.

The amount of salt required to keep the Z-value of the first inflection at 1.143 was determined by titrating 0.005 - 0.09M lithium molybdate in the presence of different amounts of potassium chloride. The results (Table I) were obtained by the differential method. The salt effect was apparent when the salt concentration was more than five-fold that of molybdate; even 50-fold amounts showed no interference.

TABLE I

AMOUNT OF POTASSIUM CHLORIDE REQUIRED TO KEEP THE Z-VALUE AT 1.143

Li_2MoO_4 (mole l^{-1})	*KCl (mole l^{-1})*	*Z-value*	*Li_2MoO_4 (mole l^{-1})*	*KCl (mole l^{-1})*	*Z-value*
0.09225	0.30	1.155	0.01025	0.040	1.163
	0.40	1.146		0.055	1.143
	0.50	1.143		0.55	1.143
	1.00	1.143	0.008200	0.031	1.202
0.06150	0.28	1.148		0.041	1.143
	0.35	1.143		0.41	1.143
	0.38	1.143	0.005125	0.020	1.233
	1.00	1.143		0.027	1.143
0.03045	0.10	1.150		0.40	1.143
	0.15	1.144			
	0.18	1.143			
	0.98	1.143			

Interfering ions. Cations such as lead, calcium, and silver, which precipitate molybdates, caused positive errors, because the polymerization reaction proceeded between solid and liquid, so that the reaction rate was seriously retarded and the inflection point was delayed. Hydroxide ions did not affect the detection of the end-point, because the equilibrium constant of the neutralization process is far larger than that of the polymerization process, and the heat evolved is also larger. In the course of the titration, the large inflection based on neutralization appeared first and then the inflection caused by polymerization followed first and then the inflection caused by polymerization followed. Thus, a differential determination of hydroxide and molybdate can be achieved. Anions such as WO_4^{2-}, VO_4^{3-}, VO_3^-, and CrO_4^{2-}, which are also polymerized on addition of a mineral acid, affected the titration curves for molybdate, giving positive errors.

Assay method. Commercial sodium molybdate and potassium molybdate, and other molybdates prepared by the author, were assayed by the proposed method. Table 2 shows the results obtained by the differential method and the reference thermal method. For comparison, results obtained by permanganate titration, after treatment in a Jones reductor[60] are also given. The assay of molybdate showed an accuracy, as well as precision, of 1.8% for 0.005 - 0.5M molybdate solutions.

Assay of ammonium paramolybdate

Two inflections were observed on the titration curve, based on the following reactions:

TABLE 2

COMPARISON OF RESULTS FOR DETERMINATION OF MOLYBDATES

Compound	*Sample taken (mole/200 ml)*	*Molybdenum (%)*			*s_r (%)*	*Accuracy (%)*
		Jones method	*Reference method*[a]	*Differential method*[a]		
$Na_2MoO_4 2H_2O$	0.10110	39.5_4	39.6_1	39.6_1	0.1_1	−0.07
	0.01011	39.3_9	39.6_0	39.6_1	0.3_3	−0.07
	0.00101	38.8	39.6	39.6	0.5	−0.09
$K_2MoO_4 5H_2O$	0.10052	29.0_5	29.2_1	29.2_1	0.1_5	−0.03
	0.01005	28.8_7	29.2_1	29.2_1	0.3_0	−0.03
	0.00105	28.0	28.9	29.1	0.4	−0.4
$MgMoO_4 \cdot 2H_2O$	0.10204	47.7_0	47.7_4	47.7_4	0.1_4	−0.01
	0.01020	47.0_6	47.6_7	47.7_0	0.1_8	−0.09
	0.00102	44.6	47.1	47.4	0.8	−0.7
$((CH_3)_4N)_2MoO_4 \cdot 2H_2O$	0.09989	29.4_2	29.4_2	29.4_2	0.2_0	−0.01
	0.00999	29.0_6	29.3_3	29.4_0	0.3_1	−0.08
	0.00100	25.5	29.2	29.3	0.6	−0.4
$((C_2H_5)_4N)_2MoO_4 \cdot 2H_2O$	0.10152	21.8_7	21.9_0	21.9_0	0.1_8	−0.05
	0.01015	21.6_5	21.8_4	21.8_7	0.2_6	−0.09
	0.00102	20.5	21.0	21.5	1.0	−1.8

[a] Mean of seven determinations.

TABLE 3

COMPARISON OF RESULTS FOR DETERMINATION OF AMMONIUM PARAMOLYBDATE

Sample taken (mole/200 ml)	*Molybdenum (%)*				
	Burns et al.[10] *method*	*Differential method*[a]			
		1st inflection	*s_r (%)*	*Accuracy (%)*	*2nd inflection*
0.01388	54.3_1	54.3_1	0.08	−0.01	54.3_2
0.01057	54.3_1	54.3_1	0.1_1	−0.01	54.3_2
0.00763	54.5	54.3	0.2	−0.03	54.3
0.00472	55.0	54.2	0.2	−0.2	54.3
0.00139	56.1	54.1	0.3	−0.4	54.3
0.00106	58.7	54.1	0.3	−0.4	54.4
0.00076	—	54	0.4	−0.6	55
0.00047	—	54	0.6	−0.6	57
0.00014	—	53	1.5	−2.4	60

[a] Mean of seven determinations.

$(NH_4)_6Mo_7O_{24} + 8NaOH = 3(NH_4)_2MoO_4 + 4Na_2MoO_4 + 4H_2O$ (1st inflection)

$(NH_4)_2MoO_4 + 2NaOH = Na_2MoO_4 + 2NH_4OH$ (2nd inflection)

The values biven in Table 3 were calculated by means of the above equations from the amount of sodium hydroxide consumed. The precision and accuracy of the determinations based on the first inflection were maintained invariably even when the concentration of the molybdate was low, but results based on the second inflection depended on the molybdate concentration, because of the ambiguous end-point at low concentrations (Fig.4). Ammonium paramolybdate in concentrations between 0.0007 and 0.07M could be determined with an accuracy and precision usually better than 2.4%. The pH titrations suggested by Burns *et al.*[53] were also tested; the results (Table 3) showed that molybdate could be determined in the 0.005 - 0.07M range, but with lower concentration, no inflection was observed.

Assay of molybdic acid and molybdenum trioxide.

Molybdic acid and molybdenum trioxide react with sodium hydroxide as follows:

$2NaOH + MoO_3 = Na_2MoO_4 + H_2O$

$2NaOH + MoO_3H_2O = Na_2MoO_4 + 2H_2O$

The values biven in Table 4 were calculated according to the above equations. Molybdic acid was found to have a lower content of molybdenum than the theoretical value (59.92%), and the sample seemed to be contaminated with ammonia; this low content was confirmed by the pH titration of Burns *et al.*[53] and by the gravimetric method.

TABLE 4

COMPARISON OF RESULTS FOR DETERMINATION OF MOLYBDENUM TRIOXIDE AND MOLYBDIC ACID

Compound	*Sample taken* (*mole/20 ml*)	*Molybdenum (%)*			*s_r* (*%*)	*Accuracy* (*%*)
		Jones method	*Gravimetric method*[a]	*Differential method*[a]		
MoO_3	0.01023 0.01011 0.01033 0.00989 0.01024 0.00978 0.00973	66.6_0	66.6_1	66.6_1	0.2_7	−0.02
	0.00115 0.00136 0.00103 0.00125 0.00104 0.00111 0.00217	65.1	66.3	66.4	0.4	−0.4
	0.00026 0.00028 0.00023 0.00035 0.00027 0.00030 0.00031	60	58	66	0.9	−0.9
$MoO_3 \cdot H_2O$	0.01132 0.01133 0.01006 0.01089 0.00958 0.00972 0.00894	54.2_5	54.3_2	54.1_7	0.3_8	−9.6
	0.00036 0.00035 0.00048 0.00039 0.00027 0.00029 0.00030	42	37	54	1.0	−9.9

[a] Mean of seven determinations.

The assay of molybdic acid and molybdenum trioxide could be achieved by thermometric titration with a precision of 1.0% or better.

DETERMINATION OF ALIPHATIC AND CYCLOALIPHATIC AMINES BY THERMOMETRIC TITRATION

Summary

Thermometric titration of aliphatic and cycloaliphatic amines with acids was studied in nonaqueous solvents. Differentating thermometric titration of three component mixtures of primary, secondary and tertiary amines with acids also studied in nonaqueous solvents. Hydrochloric acid and perchloric acid as titrants and dioxane, methylisobutylketone, acetonitrile, methylcellosolve, isopropylalcohol, G-H solvent and glacial acetic acid as solvents were used. The amine mixtures were pretreated by Siggia's method(Salicylaldehyde-acetic anhydride addition method).

Precisions were 0.5% and 0.4% for titrations 0.004M and 0.02M amines, respectively. It was found that the most feasible titrations of amine mixtures can be accomplished by a combination of dioxane as solvent and perchloric acid as titrant. By this combination, precisions for titrations of primary amines, primary plus secondary amines, secondary plus tertiary amines and tertiary amines were 0.8%, 0.7%, 0.8%, and 0.5%, respectively and accuracies 0.8%, 0.8%, 0.5%, and 0.4%, respectively. It was found that both acid-catalyzed hydrolysis of acetic anhydride(exothermic) and acid-catalyzed reaction of salicylaldehyde to acetal(exothermic) are useful for the end-point detection of thermometric titration.

Introduction

Potentiometric method as well as acid-base indicators are generally employed for the indication of the end point of the titration of amines in nonqueous solvents with acids. In the potentiometric titration s suitable indicator electrode should be chosen, because the results are apt to be affected by the dielectric constant of the solvent used, the kind of the titrant, and the substance to be titrated. Particularly in the solvent of lower dielectric constant the liquid junction potential between the refernce electrode and the solvent is enormously large and the instability of the potential brings poor reproducibility of the method[62]. In the acid-base indicator method, an indicator should also be selected for a solvent to be used and a sample to be determined. In the latter method a slight contamination with water in the solvent remarkably reduces the sharpness of the colour change response[63].

In contrast to the above methods the thermometric titration method, in which the end point is determined by the temperature change caused by the heat of the reaction, is not affected by dielectric constant of solvent used. Employing the high-sensitive thermistor and the differential thermistor a sample solution of low concentration have become to be titrated precisely[57].

In this thermometric titration the nonaqueous system is of greater advantage than the aqueous system since the organic solvents are of lower specific heat than water.

Aliphatic amines and cycloaliphatic amines have been found to be titrated directly with acid by the potentiometric method[64] or the acid-base indicator method[65], and , however, mixtures of primary, secondary and tertiary amines could not be titrated differentially with acid, and , therefore, some pre-treatment was necessary to reach the end. Siggia *et al.*[66] recommended a pre-treatment, "salicylaldehyde-acetic anhydride addition method", prior to the differential titration of primary, secondary and tertiary amines with hydrochloric acid potentiometrically in the solvent mixture of ethylene glycol-isopropanol in 1 : 1. Huber[67], after the same pre-treatment of a sample as Siggia *et al.* described, performed the differential titration of amines with perchloric acid in the solvent mixture of dioxane-glacial acetic acid-acetonitrile.

On the other hand, Forman *et al.*[68,69] described the thermometric titrations of aliphatic amines and cycloaliphatic amines with hydrobromic acid in acetonitrile, and also Keily *et al.*[70] those with perchloric acid in glacial acetic acid, and Vaughan *et al.*[71] examined the titration of amines with anhydrous hydrogen chloride in acetone, nitrobenzene or glacial acetic acid. However, the differential determination of amines in their mixture has never been investigated.

Experimental

Apparatus and procedure.

As a thermometric titrator, a trial apparatus of TOA Electric Co., to be saled as TMT-1A type was employed and the EPR10A recorder of the same company was attached to draw titration curves. The titration curves of differential titrations and reference titration were recorded on charts in the same manner as described previously.[57] *Rate of titration was 6ml/min. and chart driving speed was either 60mm/min or 180mm/min. The volume of sample solution was 10.0ml in every case.*

If solvents of a sample solution and a titrant differ from each other, the heat of mixing is evolved with a failure to observe the end point of the titration, therefore the identical solvent was used in the titration system. All the titrations were carried out at room temperature kept at 18 -22°C.

Reagents

Standard hydrochloric acid(0.1N). A 8.3ml of 35% hydrochloric acid of guaranteed grade reagent of Wako Chemicals Co. was dissolved in an appropriate solvent and the volume was made 1l with the same solvent. The solution was allowed to stand for a long time till the temperature equilibrium was reached between the solution and the atmosphere. 1,3-diphenylguanidine was preferred as a standard substance and its solution of a definite concentration was used to standardize the hydrochloric acid solution by the ordinary method, using crystal violet as an indicator.

Standard perchloric acid(0.1N). A 8.5ml of 70% perchloric acid of guaranteed grade reagent of the same manufacturer was dissolved in an appropriate solvent to make a 1l solution, and the solution was put aside till the temperature of the solution reached to that of the room. When glacial acid was used as a solvent, 15ml of acetic anhydride was added together and the solution was allowed to stand over night. The standardization of the solution was done same as in the case of the hydrochloric acid solution.

Solvents. All solvents were of the guaranteed grade reagent of the same company. Dioxane was purified with sodium hydroxide by Siggia's method[72]. Methylisobutylketone(MIBK), acetonitrile, isopropanol(IPA), methyl cellosolve, ethyleneglycol, and glacial acetic acid were purified by the conventional methods[73]. G-H solvent was consisted of ethyleneglycol and IPA in 1:1 volume ratio.

Sample amines. Commercial guaranteed reagents of n-butylamine di-n-butylamine, tri-n-butylamine, n-hexylamine, di-n-amylamine, tri-n-octylamine, cyclohexylamine, N-methylcyclohexylamine, N,N-dimethylcyclohexylamine, diethanolamine, triethanolamine, piperidine, morphorine, were used as samples respectively and their purities were examined by the titrations of them with perchloric acid in glacial acetic acid solvent, using crystal violet as an indicator.

Sample solutions. Each amine was dissolved in solvents to make 0.01M for primary amines, 0.01M for secondary amines, 0.02M for tertiary amines, respectively.

Sample solutions for the determination of the sum of secondary and tertiary amines. In a 30ml solvent 0.001mol of primary amines, 0.001mol of secondary amine, and 0.002mol of tertiary amine were all dissolved together, and 3ml of salicylaldehyde was then added; the solution was allowed to stand for 30 minutes to convert the primary amine into imine(Schiff base), and then the total volume was made up 100ml by adding the solvent.

Sample solutions for the determination of the tertiary amines. In a 30ml solvent 0.001mol of primary amine, 0.001mol of secondary amine, and 0.002mol of tertiary amine was dissolved together, and 3ml of acetic anhydride was added; the solution was allowed to stand for twenty minutes to convert the primary and the secondary amines into amines, and then the solution was made up to 100ml by adding the solvent.

1,3-diphenylguanidine. Guaranteed reagent of Tokyokasei Co. was purified by double recrystallization from toluene and from ethanol, and dried at 110°C.

Salicylaldehyde and acetic anhydride. The commercial guaranteed reagents were purified by distillation.

Results

Titration curves for various amines

Titration curves with standard hydrochloric acid solution. Using dioxane, MIBK, acetonitrile, and IPA as solvents, 0.02M *n*-butylamine, 0.02M triethanolamine and 0.004M N,N-dimethylcyclohexylamine were titrated with 0.1N hydrochloric acid standard solution. Titration curves obtained are shown in Figs 1, 2, and 3, respectively, in which the reference curve and the differential curve are shown together for each case, and the following results should be noted.

(1) By the differential method distinct end point could be observed on the titration curves for amines of so low concentration as about 0.004M(Fig.3).

(2) By the refernce method distinct end point appeared on the curve for amines of 0.02M, but the end point became ambiguous for lower concentration as 0.004M of amines since heat of dilution of hydrochloric acid in IPA caused a steep ascension of the titration curve after the end point. The same effects were observed when using methyl cellosolve or G-H solvent, not shown in Figure. When MIBK or dioxane were employed as solvents the refernce method could give relatively distinct and sharp end point. This may be attributted to the endothermic heat of dilution of hydrochloric acid in these

solvent as the titration curve descends after the end point, giving a sharp acute angle at that point. In glacial acetic acid hydrochloric acid shows its heat of dilution slightly endothermic[69], therefore when using this solvent a sharp end point could also be observed.

(3) Precipitate of chlorides appeared when 0.02M triethanolamine was titrated with hydrochloric acid in dioxane or acetonitrile. In these cases titration curve had a steep ascending part nearly upright that arose from combined heat of neutralization and precipitation (Figs. 2a and 2c). But in IPA solvent, the precipitate appeared eventually near the end point and, therefore, the end point indication became obscure(Fig.2d).

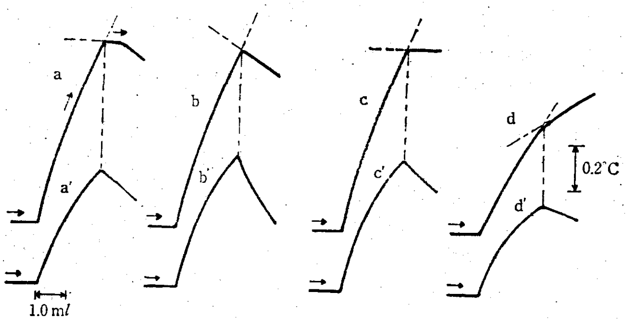


Fig.1 Thermometric titration curves of 0.02M *n*-butylamine in various solvents with 0.1N hydrochloric acid standard solution.
(a,b,c,d; reference method, a',b',c',d';differential method)
a,a' : in dioxane, b,b': in MIBK, c,c': in acetonitrile, d,d': in IPA.

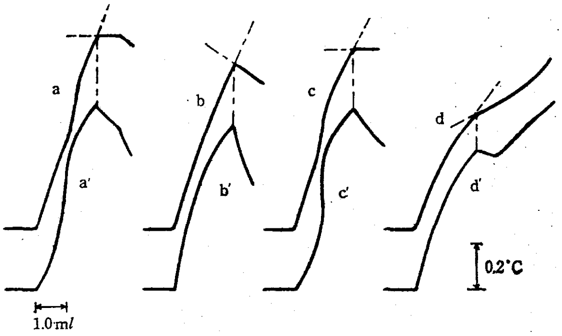


Fig.2 Thermometric titration curves of 0.02M triethanolamine in various solvents with 0.1N hydrochloric acid standard solution.
(a,b,c,d; reference method, a',b',c',d'; differential method)
a,a': in dioxane, b,b': in MIBK, c,c': acetonitrile, d,d': in IPA.

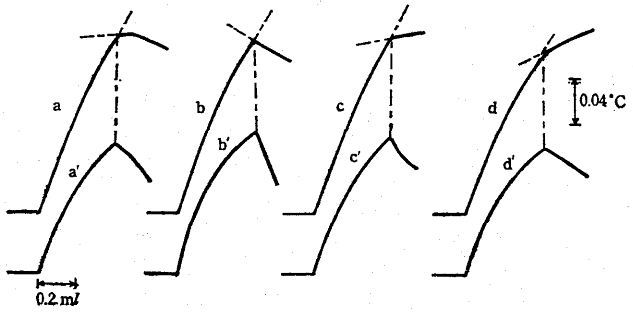


Fig.3 Thermometric titration curves of 0.004M N,N-dimethylcyclohexylamine in various solvents with 0.1N hydrochloric acid standard solution.
(a,b,c,d; reference method, a',b',c',d'; differential method)
a,a': in dioxane, b,b': in MIBK, c,c': in acetonitrile, d,d': in IPA.

Titration curves with standard perchloric acid. In dioxane, MIBK, and IPA, 0.004M N-methylcyclohexylamine was titrated with 0.1N perchloric acid standard solution by both differential and reference method. The titration curves obtained are shown in Fig.4, from which the following evidences can be revealed.

(1) Like the titrations with hydrochloric acid the titration curves of the differential method gave their definitive end points but of sharpness inferior to those in Fig.3.

(2) In the case of the reference method, heat of dilution of perchloric acid displayed its effect in MIBK and IPA as the titration curve rose further after the end point, resulting the uncertain indication of the inflection of the curve. In methyl cellosolve and G-H solvent the same effect could be observed, but in dioxane and in glacial acetic acid, as not shown in figure, sharp end point could be observed since heat of dilution of perchloric acid did scarcely evolve.

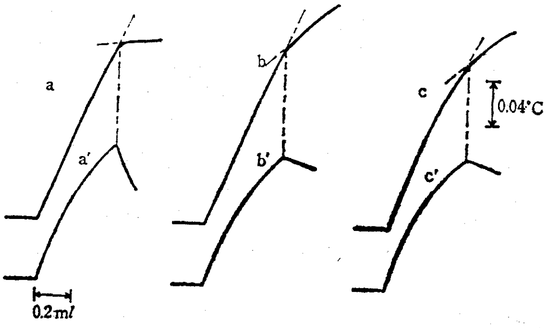


Fig.4 Thermometric titration curves of 0.004M of N-methylcyclohexylamine in various solvents with 0.1N perchloric acid standard solution. (a,b,c; reference method, a',b',c'; differential method)
a,a': in dioxane, b,b': in MIBK, c,c': in IPA.

Precision and accuracy of the determination of individual amines.

Precision(coefficient of variation) and accuracy (relative error%) of the determination of individual amines when the differential titrations were carried out in dioxane with 0.1N hydrochloric acid solution or perchloric acid solution for 0.004M amines are listed respectively in Table 1, and for 0.02M amines in Table 2. From the Tables the following results can be summarized.

(1) Both precision and accuracy of the determination of 0.02M amines fall within 0.4% in every case.

(2) The precision and the accuracy of the determination of 0.004M amines fall within 0.5% of the former and 0.8% of the latter.

(3) Precision and accuracy were not affected by the precipitates appearing during the titration. Precision of 0.9% and accuracy of 1.0% could be obtained, those not noted in the Table, when 0.02M triethanolamine was titrated with standard hydrochloric acid in IPA.

(4) No difference of the precision and the accuracy could be found between the titrations with hydrochloric acid and those with perchloric acid. When solvents other than dioxane were used equal precision and accuracy were obtained.

Table 1 Precision and accuracy obtained in the titration of various amines (0.004M) in dioxane.

Amine (0.004M)	With HCl		With $HClO_4$	
	Precision (%)	Accuracy (%)	Precision (%)	Accuracy (%)
n-Buthylamine	0.3_2	0.6_2	0.3_3	0.7_1
Di-*n*-buthylamine	0.2_8	0.5_3	0.2_5	0.5_1
Tri-*n*-buthylamine	0.3_3	0.4_1	0.3_3	0.4_1
Di-*n*-amylamine	0.3_3	0.5_2	0.3_7	0.5_0
Cyclohexylamine	0.2_2	0.5_5	0.3_0	0.5_2
N-methylcyclo-Hexylamine	0.3_3	0.4_5	0.3_4	0.4_3
N,N-dimethylcyclo-Hexylamine	0.3_7	0.4_6	0.3_8	0.4_6
Diethanolamine	0.3_2	0.7_0	0.40	0.7_1
Triethanolamine	0.3_9	0.7_5	0.3_8	0.7_5
Morphorine	0.4_1	0.3_1	0.3_8	0.3_2
Piperidine	0.4_0	0.3_1	0.3_5	0.3_1

Table 2 Precision and accuracy obtained in the titration of various amines (0.02M) in dioxane.

Amine (M)	With HCl		With $HClO_4$	
	Precision (%)	Accuracy (%)	Precision (%)	Accuracy (%)
n-Buthylamine	0.1_8	0.1_9	0.1_4	0.1_9
Di-*n*-amylamine	0.1_8	0.1_3	0.1_6	0.1_3
Cyclohexylamine	0.1_3	0.1_4	0.1_5	0.1_5
Triethanolamine	0.3_4	0.2_8	0.2_8	0.2_9
Morphorine	0.1_3	0.1_8	0.1_5	0.1_5
Piperidine	0.1_8	0.1_6	0.1_5	0.1_5

Titration curves for amine mixtures.

Titration curves for amine mixtures with standard hydrochloric acid solution. A mixture consisting of 0.01M cyclohexylamine, 0.01M N-methylcyclohexylamine and 0.02M N,N-dimethylcyclohexylamine was titrated with 0.1N hydrochloric acid in dioxane, and the titration curves are shown in Fig.5, in which 5a shows the inflection point for the total amines, 5b shows two inflection points, the first for the secondary plus the tertiary amines and the second for the primary amine(Schiff base), and 5c that for the teriary amine. Similar curves were obtained for the titrations in acetonitrile and in IPA. Fig.6 shows the curves for the same titrations in methyl cellosolve and similar curves were also obtained in G-H solvent. From Figs. 5 and 6 the followings may be concluded.

(1) When dioxane, acetonitrile, and IPA were used respectively as a solvent, the titration curves by the differential method for pre-treated amine mixture showed their distinct end points, one for the secondary plus tertiary amines and the other for the primary amine; by the reference method the inflection for primary amine was somewhat indistinct.

(2) When methyl cellosolve or G-H solvent was used the inflection for the secondary plus tertiary amines first

appeared on the curve, followed by that(the arrow in 6b') for primary amine(Schiff base) and by re-ascension of the curve. This ascension of the curve after the second inflection means the heat of reaction between salicylaldehyde in excess and hydroxyl group of the solvent by the catalytic action of hydrochloric acid, resulting acetal.

When glacial acetic acid was used as a solvent, only the inflection for the total amines could be observed, but not for the primary plus tertiary amines as well as for tertiary amine.

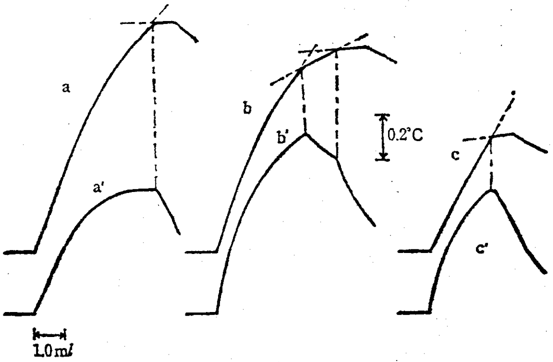


Fig.5 Thermometric titration curves of amine mixture in dioxane with hydrochloric acid standard solition.
(a,b,c; reference method, a',b',c'; differential method)
Amine mixture: 0.01M cyclohexylamine+0.01M N-methylcyclohexylamine+ 0.02M N,N-dimethylcyclohexylamine.
a,a'; for the total amines, b,b'; for the secondary plus the tertiary amines, c,c'; for the tertiary amine.

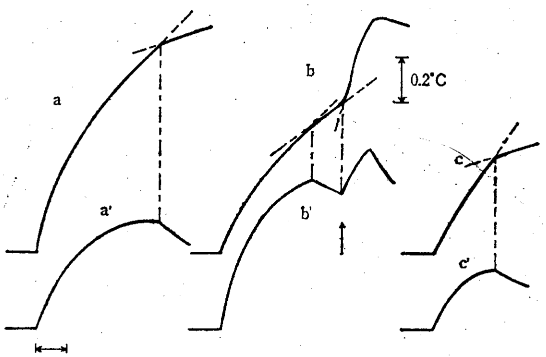


Fig.6 Thermometric titration curves of amine mixture in methyl cellosolve with hydrochloric acid standard solution.
(a,b,c; reference method, a',b',c'; differential method)
Amine mixture: 0.01M cyclohexylamine+0.01M N-methylcyclohexylamine+ 0.02M N,N-dimethylcyclohexylamine.
a,a'; for the total amines, b,b'; for the secondary plus the tertiary amines, c,c'; for tertiary amine.

Titration curves for amine mixtures with standard perchloric acid solution. A mixture consisting of 0.01 M cyclohexylamine, 0.01M N-methylcyclohexylamine and N,N-dimethylcyclohexylamine was titrated with 0.1N standard perchloric acid solution in dioxane, and the titration curves are shown in Fig.7. Similar titration curves were also obtained in acetonitrile as a solvent. Titration curves in IPA, methyl cellosolve and G-H solvent were similar to those in where hydrochloric acid was used as a titrant. From Fig.7 the followings may be summarized.

(1) When dioxane or acetonitrile were used as solvents,

two inflection points appeared on the titration curves of the samples treated for tertiary amine; the first corresponded to the amount of tertiary amine taken and the second to that of primary plus secondary amines, namely to the amount of amide, as shown by the arrow on 7c'. After this second inflection steep rise of the curve was found; that might be due to the heat of reaction of acid-catalyzed hydrolysis of acetic anhydride existing in excess[74,75]. In this system the inflection for the primary plus secondary amines could be observed distinctly as shown above and this seemed an outstanding characteristics of the method since none of other methods could respond.

When glacial acetic acid was used as a solvent, only as inflection point corresponding to the total amount of mixed amines, and, moreover, the sample treated for tertiary amine gave a steep jump of the titration curve appearing at the inflection point owing to the acid-catalyzed hydrolysis of acetic anhydride.

Precision and accuracy of the determination of amine mixtures.

In Tables 3 and 4, the precision and accuracy are listed for the titration of amine mixtures, consisting of *n*-butylamine, di-*n*-butylamine and tri-*n*-butylamine, of *n*-hexylamine, di-*n*-amylamine and tri-*n*-octylamine,

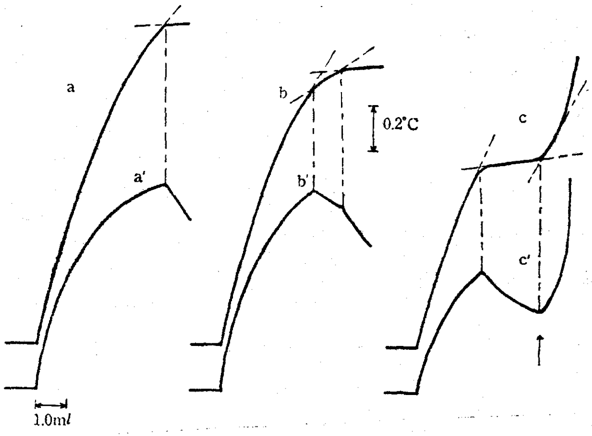


Fig.7 Thermometric titration curves of amine mixture in dioxane with perchloric acid standard solution.
(a,b,c; reference method, a',b',c'; differential method)
Amine mixture: 0.01M cyclohexylamine+0.01M N-methylcyclohexylamine+ 0.02M N,N-dimethylcyclohexylamine.
a,a'; for the total amines, b,b'; for the secondary plus the tertiary amines, c,c'; for the tertiary amine.

and of cyclohexylamine, N-methylcyclohexylamine, and N,N-dimethylcyclohexylamine with perchloric acid standard solution in dioxane or methyl cellosolve. These data were obtained by calculating from the titrant volumes of the end points read directly on the titration curves. The following conclusions may be derived from these data.

(1) Total amounts of amines could be determined to precision and accuracy both within 0.5%, for samples of amine mixture.

Table 3 Precision and accuracy obtained in the titrations of pre-treated amine mixture in dioxane with perchloric acid standard solution.

	Total amine		Primary amine		Prim.+ secon. amine		Secon.+ terti. amine		Tertiary amine	
Amine mixyure	Preci. (%)	Accur. (%)	Preci. (%)	Accur. (%)	Preci. (%)	Accur. (%)	Preci. (%)	Accur. (%)	Preci. (%)	Accu. (%)
n-Butylamine Di-*n*-butylamine Tri-*n*-butylamine	0.2_5 (0.4_9)* (0.4_2)**	0.4_1 (0.6_8)* (0.6_8)**	0.8_0	0.5_7	0.6_5	0.7_7	0.4_5	0.4_2	0.3_2	0.3_0
n-Hexylamine Di-*n*-amylamine Tri-*n*-octylamine	0.2_0 (0.4_2)* (0.4_0)**	0.4_5 (0.5_9) (0.6_9)	0.7_7	0.7_0	0.5_9	0.7_0	0.4_0	0.4_0	0.4_0	0.2_0
Cyclohexylamine N-methylcyclohexylamine N,N-dimethylcyclohexylamine	0.2_2 (0.4_5)* (0.4_3)**	0.4_5 (0.5_5)* (0.6_6)**	0.7_7	0.7_6	0.6_3	0.7_1	0.4_2	0.4_6	0.4_1	0.3_1

* are obtained from sample for the secondary plus the tertiary amines.

** are obtained from saple for the tertiary amine.

Table 4 Precision and accuracy obtained in the titrations of pre-treated amine mixture in methyl cellosolve with perchloric acid standard solution.

	Total amine		Primary amine		Sec.+ tert. amines		Tertiary amine	
Amine mixture	Precision (%)	Accuracy (%)	Precision (%)	Accuracy (%)	Precision (%)	Accuracy (%)	Precision (%)	Accuracy (%)
n-Butylamine								
Di-*n*-butylamine	0.3_0	0.4_5	0.5_5	0.3_0	0.3_8	0.2_0	0.3_5	0.3_0
Tri-*n*-butylamine	(0.4_4)*	(0.6_6)*						
n-Hexylamine								
Di-*n*-amylamine	0.3_1	0.4_4	0.5_2	0.3_1	0.3_0	0.2_1	0.4_0	0.2_0
Tri-*n*-octylamine	(0.4_0)*	(0.6_0)*						
Cyclohexylamine								
N-methylcyclohexylamine	0.3_8	0.4_8	0.5_2	0.3_8	0.2_9	0.2_8	0.4_0	0.2_0
N,N-dimethylcyclohexylamine	(0.4_0)*	(0.5_8)*						

* are obtained from sample for the secondary plus the tertiary amines.

(2) When the pre-treated samples to determine particularly the secondary plus the tertiary amines were submitted to this method, total amounts of amines could be estimated to precision within 0.5% and accuracy within 0.7%; the amounts of the secondary plus the tertiary amines fell within 0.6% of both precision and accuracy; the amounts of the primary amine fell within 0.9% of both precision and accuracy; all were determined differentially. As being not shown in Tables, when MIBK was used as a solvent, the determined values of the secondary plus the tertiary amines were so bad as its precision be 11.0 % and accuracy 6.0%, and therefore, MIBK was found unsuitable for the differentiating titration of amines.

(3) When a sample pre-treated particularly for determination of the tertiary amine was submitted to the titration in dioxane, both precision and accuracy for total amines fell within 0.5%, those for the primary plus the secondary amines did within 0.8%, and those for the tertiary amine did within o.5%, by the differential method.

DIFFERENTIATING TITRATION OF AROMATIC AMINES BY THERMOMETRIC TITRIMETRY

Summary

By the thermometric titration the determination of mixtures of primary, secondary and tertiary amines has been achieved. For the determination of mixture of amines perchloric acid was found to be the most preferable titrant and isopropyl alcohol, G-H solvent and methyl cellosolve were available as the solvents in this titration. The precision and accuracy of the method for each case were as follows: for total amount of amines in the mixture, within 0.7%; primary amines, within 1.0%; secondary amines, within 1.0%; tertiary amines, within 0.5%; secondary plus tertiary amines, within 0.9%.

The order of differentiating ability of the solvents was examined with the isomer of phenylenediamine. Hydrochloric acid and perchloric acid as titrants were used. In the titration with hydrochloric acid the order was:

isopropyl alcohol < glacial acetic acid, G-H solvent < dioxane < methyl cellosolve < acetonitrile, methyl isobutyl ketone ,

in increasing order and on the titration with perchloric acid the order was:

isopropyl alcohol < glacial acetic acid < methyl cellosolve, G-H solvent < dioxane < acetonitrile, methyl isobutyl ketone,

in increasing order.

Introduction

The differential determination of aromatic primary, secondary and tertiary amines, abbreviatted as amine-mixture hereinafter in this paper, can be achieved potentiometrically after the sample has been treated by salicylaldehyde or acetic anhydride addition method in a similar manner as for aliphatic amine mixtures. In this case, hydrochloric acid or perchloric acid is used as a titrant and a mixed solvent of ethyleneglycol and isopropyl alcohol or that of dioxane and acetonitrile is used as a medium[66,67].

A number of reports has been published about the thermometric titration of individual aromatic amines[76], but none of the reports for the amine-mixture have been found.

In the preceding chapter[58] the author worked on the differentiating thermometric titration of aliphatic amine-mixtures and cycloaliphatic amine-mixtures, taking advantages of the exothermic properties of acid-catalyzed acetal formation reaction of salicylaldehyde as well as acid-catalyzed hydrolysis of acetic anhydride. These exothermic reactions have been applied again in the present study for the thermometric titration of the aromatic amine-mixture in non-aqueous solvent, using the differential thermistor as tools.

When differentiating titration of amines would be achieved in non-aqueous solvents, the differentiating ability of the solvent seems to be a significantly important property. The differentiating ability of solvents can usually be interpreted from the results of potentiometric titration in various solvents as follows: One, the dissocitation constant of a substance in aqueous solution pK(H_2O) is plotted against the difference (ΔHNP) between half neutralization potential in a solvent of interest of a definite standard substance and that of the same substance, and the slops of these linear plots are compared with each other[77,78], and the other, potentiometric titration curves in a solvent of interest of two substances, being pK(H_2O) of them close to each other, are compared[79]. However, the order of the differenciating ability of organic solvents has never been determined by the thermometric titration. Since thermometric titrations using differential thermistor seemed to be well suited for the differntiating titrations[57,58], the order of the differenciating ability was attempted to be determined by this method. For the purpose, three isomers of phenylenediamine were preferred and they were titrated with standard hydrochloric acid or perchloric acid in each of seven solvents. The acid-base equivalence points of each isomer are as follows[80];

Isomer	The first $pK_B(H_2O)$	The second $pK_B(H_2O)$
o-phenylenediamine	9.53	>12
m-phenylenediamine	9.12	11.35
p-phenylenediamine	7.92	10.71

In order to determine the aromatic amine-mixtures differentially the thermometric titration was examined elaborately and this method was found being superior to usual potentiometric titration from a standpoint of its rapidity and simplicity, accompanying excellent precision and accuracy.

Experimental

Apparatus and procedure

A thermometric titrator and a recorder was same as those previously described. The titration cell was a 50ml Teflon beaker and the titrating rate was 5.88ml/min.. Recording chart was driven at the rate 60mm/min. or 180mm/min.. All titrations were performed with each 10.0ml sample solution, and room temperature kept at 18 - 20°C. The identical solvent was used to make standard solution of titrant and sample solutions.

Reagents

Standard hydrochloric acid(0.1N). A 8.9ml portion of 35% hydrochloric acid of guaranteed reagent grade of Wako Chemicals was diluted to 1l with a solvent, and the solution was allowed to stand till the solution temperature and room temperature reached to equilibrium. This acid solution was standardized with 1,3-diphenylguanidine as a primary standard by thermometric titration.

Standard perchloric acid(0.1N). A 9.0ml portion of 70% perchloric acid of guaranteed reagent grade of the same company was diluted to 1l with a solvent and the solution was put aside to equilibrate the temperature between the solution and the room. When glacial acetic acid was used as a solvent, 15ml acetic anhydride was added and the solution was stood over night. The standardization was same as for hydrochloric acid solution.

Solvents. Solvents used were all of the guranteed reagent grade of Wako Chemicals. Dioxane was further purified by treating it with sodium hydroxide according to Siggia's method[72], methyl isobutyl ketone(MIBK) was by the method of Bruss et al[81], and acetonitrile by the method of Forman et al[69]. Isopropyl alcohol(IPA), methyl cellosolve, ethyleneglycol and glacial acetic acid were purified by the conventional method[73] respectively. G-H solvent was composed by mixing ethyleneglycol and IPA in 1:1 volume ratio.

Amines. Aniline, N-methylaniline, N,N-dimethylaniline, α-naphthylamine, N-methyl-α-naphthylamine, N,N-dimethyl-α-naphthylamine, o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, phenylethanolamine, phenyldiethanolamine, and quinoline, were all commercial guranteed reagent grade, and their purity was assayed respectively by the method of Fritz et al[82], using neutral red as indicator.

Sample solution for determing total amounts of amine-mixture. Sample solutions were prepared by mixing individual amine solutions with solvent as to be primary, secondary and tertiary amines in 0.01M, 0.01M and 0.02M respectively.

Sample solution for determing secondary plus tertiary amines. In 20ml of a solvent 0.001mol primary, 0.001mol secondary and 0.002 mol tertiary amines were dissolved respectively and 5ml of salicylaldehyde was added in the solution, followed by standing for thirty minutes to convert primary amine into imine(Schiff base), and the volume was made up to 100ml by adding the solvent.

Sample solution for determing tertiary amine. In 20ml of a solvent 0.001mol primary, 0.001mol secondary and 0.002mol tertiary amines were dissolved respectively and 5ml of acetic anhydride was added in the solution, following by standing for twenty minutes to convert primary and secondary amines into amide , and the volume was made up to 100ml by adding the solvent.

Both salicylaldehyde and acetic anhydride were of guranteed reagent grade and purified by distillation.

Results and discussion

Titration curves for phenylenediamine and differentiating ability of solvents.

Typical titration curves of *o*-phenylenediamine with standard hydrochloric acid in various solvents are shown in Fig.1, 1a shows the titration curves in dioxane or MIBK, on which the first and the second equivalence points appear distinctly; whereas, 1b shows the curve in glacial acetic acid, only the second equivalence point can be observed, 1c is the curve in IPA, methyl cellosolve or G-H solvent, only the first inflection is given.

On the other hand, titration curve of the amine with standard perchloric acid have two distinct inflection points as can be seen in 1d. The ascending curve after the second equivalence point seems to be attributed to exothermic heat of dilution of perchloric acid into MIBK. In acetonitrile the first and the second equivalence points could also be observed, but in solvent other than the above two the first equivalence point could be given merely. The experimental results obtained not only for *o*-phenylenediamine but for *m*- and *p*-isomers are summarized in Table 1.

From Table 1 the following facts may be pointed out when hydrochloric acid was used as a titrant:

(1) In dioxane the first and the second equivalence points of *o*-phenylenediamine could be differentially estimated, but not *p*-phenylenediamine. However, in MIBK or acetonitrile, the first and the second equivalence points of both *o*- and *p*-phenylenediamines could be differentially estimated, therefore, the last two solvents

have their differentiating ability superior to doxane.

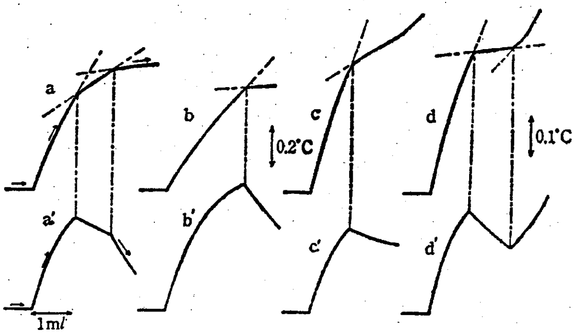


Fig.1 Thermometric titration curves of 0.02M *o*-phenylenediamine in various solvents with 0.1N hydrochloric acid standard solution or 0.1N perchloric acid standard solution.
(a,b,c,d; reference method , a',b',c',d'; differential method)
a,a': in dioxane with HCl, b,b': in acetonitrile with HCl, c,c': in IPA with HCl, d,d': in MIBK with $HClO_4$.

(2) In IPA, the first equivalence point of *m*-phenylenediamine ($pK_B(H_2O)$ 9.12) could be oberved, but the second($pK_B(H_2O)$ 11.35) could not be. Nevertheless, in G-H solvent that is a mixture of IPA and ethyleneglycol the second equivalence point could be found. From this fact ethyleneglycol might be said more acidic than IPA. In G-H solvent weak basic amines of their $pK_B(H_2O)$ around 10.7 could be differentially titrated .

(3) In methyl cellosolve the first and the second equivalence points of *p*-phenylenediamine could be differentially determined and, therefore, the differentiating titrations could be performed for weak basic amines of $pK_B(H_2O)$ around 10.7 and for those having two $pK_B(H_2O)$

Table 1 Thermometric titration of phenylenediamines in various solvents.

		Solvent						
Phenylenediamine	Titrant	Dioxane	MIBK	Acetonitrile	IPA	G-H solvent	Methyl cellosolve	Glacial acetic acid
o-	HCl	1, 2	1, 2	1, 2	1	1	1	2
	$HClO_4$	1	1, 2	1, 2	1	1	1	2
m-	HCl	2	2	2	1	2	1	2
	$HClO_4$	1, 2	1, 2	1, 2	1	2	1	2
p-	HCl	1	1, 2	1, 2	-	2	1, 2	2
	$HClO_4$	1, 2	1, 2	1, 2	-	1, 2	1, 2	2

1; the first equivalence point could be found, 2; the second equivalence point could be found.

values apart above about 2.9 from each other.

From the above results from (1) - (3), the differentiating ability of the solvents in the titration with hydrochloric acid may be arranged in the following order:
IPA < glacial acetic acid, G-H solvent < dioxane < methy cellosolve < acetonitrile, MIBK.

From Table 1 the following facts may be pointed out when perchloric acid standard solution was used as a titrant.

(4) In dioxane, the second equivalence point of *o*-phenylenediamine could not be determined, but in MIBK or acetonitrile the first and the second equivalence points could be differentiated. Therefore, the differentiating ability of MIBK or acetonitrile is superior to that of dioxane.

(5) In IPA or methyl cellosolve the second equivalence point of *m*-phenylenediamine could not be determined, but could be in G-H solvent.

From the above two facts (4) and (5), the differentiating ability of solvent may be arranged in the following order:
IPA < glacial acetic acid < methyl cellosolve, G-H solvent < dioxane < acetonitrile, MIBK.

The order of differentiating ability of solvents was found to be arranged from amphoteric solvents to polar solvents in increasing order like the order obtained by the potentiometric titrations[77-79]. This order differs to some degree whether the titration was carried out with hydrochloric acid or perchloric acid, and this difference may depend upon the different acid strength of the two acids in solvents, but not upon the water content of standard acid solutions employed. This assumption was proved as follows: in the present experiments, 0.1N hydrochloric acid solution contained 0.68% water, while 0.1N perchloric acid solution 0.43% water; when glacial acetic acid was used as a solvent, acetic anhydride was added into the solutions to make the solutions free from water; when solvents were used, a small amount of water was added in the perchloric acid solution to make it to the same water content as the hydrochloric acid solution, and the titrations of amines were carried out independently with the results in good agreement with those shown in Table 1.

Titration curves of other amines

In Fig.2 titration curves of other various amines are shown. The following facts were revealed.

(1) In the titration of phenylethanolamine with hydrochloric acid in IPA no end point could be detected. Phenyldiethanolamine and quinoline gave the same uniform curves respectively. In G-H solvent phenylethanolamine

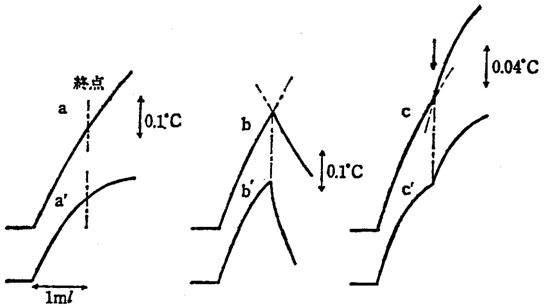


Fig.2 Thermometric titration curves of 0.02M amines in various solvents with 0.1N hydrochloric acid standard solution or with 0.1N perchloric acid standard solution.
(a,b,c; reference method, a',b',c'; differential method)
a,a': phenylethanolamine with HCl in IPA, b,b': anilne with HCl in MIBK, c,c': phenylethanolamine with $HClO_4$ in MIBK.

and phenyldiethanolamine behaved similarly. These phenomena seemed to be attributed to heat of dilution of hydrochloric acid and protolysis of the resulted salt with solvent. Therefore, it was found impossible to use IPA or G-H solvent as medium for the titration of weak amines with hydrochloric acid.

(2) On the contrary to the above solvents, MIBK was found available for the titration of weak amines with hydrochloric acid, since the titration curve descended steeply after the end point, as shown in b, owing to heat of dilution of hydrochloric acid[71]. Thus weak amines could be determined accurately.

(3) When the titration of weak amines with perchloric acid was carried out in MIBK, exothermic heat of

dilution of the acid let the curve after the end point up steeply as shown an arrow on the curve. Similar inflection point could also be found on the curve for phenylenediamine as shown d in Fig.1. From these results, heat of dilution of perchloric acid in MIBK was useful to indicate the sharp end point of titration of weak amines.

Results of the determination of individual amines.

Precision(coefficient of variation) and accuracy for when 0.01M of various amines were titrated with 0.1 N hydrochloric acid or 0.1N perchloric acid in MIBK are listed in Table 2, from which the followings are revealed.

(1) Amines of 0.01M could be determined to precision and accuracy both within 0.6%.

(2) Precision and accuracy for the titration with hydrochloric acid were almost identical either by the reference method or by differential method.

(3) The end point indication by means of the heat of dilution of perchloric acid gave results accompanying good precision and accuracy.

Aromatic primary amines are apt to react with ketones, therefore, special care has to be exercised to prevent the confusion[83]. In the present experiments MIBK solutions of aniline and of naphthylamine were prepared by dissolving the solute in the solvent and then standing for about twenty hours. These solutions were titrated to precision and accuracy within 0.6%. From this fact , only little effect was appreciable.

Table 2 Precision and accuracy obtained in the titration of various amines(0.01M) in MIBK.

	With HCl		With $HClO_4$	
Amine	Precision (%)	Accuracy (%)	Precision (%)	Accuracy (%)
Aniline	0.3_1(0.38)*	$0.4_7(0.5_0)$*	0.4_0	0.4_1
N-methylaniline	$0.3_1(0.3_5)$	$0.3_6(0.5_0)$	0.4_1	0.4_8
N,N-dimethylaniline	$0.3_1(0.3_5)$	$0.4_9(0.4_4)$	0.4_2	0.4_5
α-Naphthylamine	0.3_4	0.5_5	0.5_0	0.5_0
N-methyl-α-naphthylamine	0.3_2	0.5_5	0.5_0	0.5_0
N,N-dimethyl-α-naphthylamine	0.3_4	0.5_4	0.4_5	0.5_0
o-Phenylenediamine	0.4_8	0.5_6	0.5_5	0.5_7
m-Phenylenediamine	0.4_8	0.5_5	0.5_4	0.5_2
p-Phenylenediamine	0.5_0	0.5_5	0.5_6	0.5_2
Phenylethanolamine	$0.5_8(0.5_8)$	$0.5_8(0.6_6)$	0.5_8	0.5_9
Phenyldiethanolamine	$0.5_7(0.6_0)$	$0.5_9(0.6_8)$	0.5_8	0.5_9
Quinoline	$0.4_8(0.5_9)$	$0.5_9(0.6_8)$	0.4_5	0.5_8

* are obtained by reference method, others are obtaied by differential method.

Titration curves for amine-mixyures with hydrochloric acid.

Mixtures of aniline, N-methylaniline and N,N-dimethylaniline were prepared as described in *Sample solution* for respective purposes of titrations , and titrated with standard hydrochloric acid in dioxane. Titration curves are shown in Fig.3. Similar titration curves were also obtained for the titrations in MIBK, acetonitrile, or glacial acetic acid. The titration curves obtained in methyl cellosolve are shown in Fig.4, and those in IPA in Fig.5. From these figures the following facts can be recognized.

(1) When dioxane(Fig.3), MIBK, acetonitrile, or glacial acetic acid was used as a solvent, the titration curves, shown as b and b' in Fig.3, of samples for secondary plus tertiary amines did not give their inflection point just corresponding to the theoretical equivalence point, accompanying some positive errors. This effect was due to a small amount of aniline which had been left after the pre-treating process with salicylaldehyde of amine mixture. Moreover, the sample solution coloured light yellow in dioxane, acetonitrile, or MIBK, and tured deeper as the titration advanced till the deepest yellow appeared abruptly after the end point . This incomplete reaction of aniline with salicylaldehyde believed to be

effected by the following steps; in the condensation reaction between primary amines and carbonyl compounds aminoalcohols is first producted and the dehydration of aminoalcohols seems to be the rate-determining process; in glacial acetic acid primary amines are generally protonized and lose its reactivity of anionic reactants; therefore, the condensation reaction with carbonyl compound proceeds so slow that the reaction can not be finished within thirty minutes as recommended in this work. To make the process complete larger amounts of salicylaldehyde was added as well as the reaction time prolonged, but 100% yield of Schiff base from primary amines could not be obtained. From this result, it may be concluded that in the solvents such as dioxane, MIBK, acetnitrile and glacial acetic acid the amounts of total amines and of tertiary amine could be determined, but not secondary plus tertiary amines.

(2) Using methyl cellosolve(Fig.4), or G-H solvent as a medium distinct inflection point could not be found on the titration curves for samples for secondary plus tertiary amines. This may be response the heat is evolved simultaneously from neutralization and acetal-forming reaction during the titration, since the acid-catalyzed acetal-forming reaction proceeds gradually before the neutralization of secondary plus tertiary amines reaches

to the goal. Therefore, it is clear that evolving heat of the acid-catalyzed acetal-forming reaction of salicylaldehyde can not be applied as the means indicating end point in the titration with hydrochloric acid.

(3) In IPA(Fig.5) there were no inflection points observed on the titration curves both for total amines and for secondary plus tertiary amines. This is based on simultaneous evolution of heat of dilution of hydrochloric acid and heat of neutralization during the titration, and on the other hand, due to the increasing heat capacity of the content accompanied by increasing volume of titrant; then, the titration curve did not show its sharp inlection.

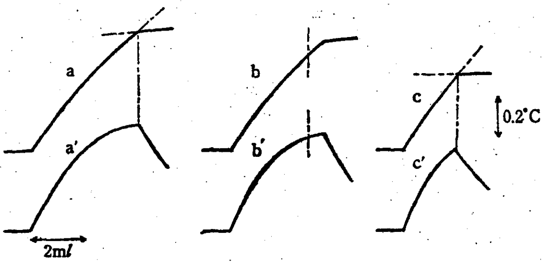


Fig. 3 Thermometric titration curves of amine mixtures in dioxane with hydrochloric acid standard solution.
(a,b,c; reference method, a',b',c'; differential method)
Amine mixture: 0.01M aniline+0.01M N-methylaniline+0.02MN,N-dimethy aniline.
a,a'; for the total amines, b,b'; for the secondary plus the tertiary amines, c,c'; for the tertiary amine.

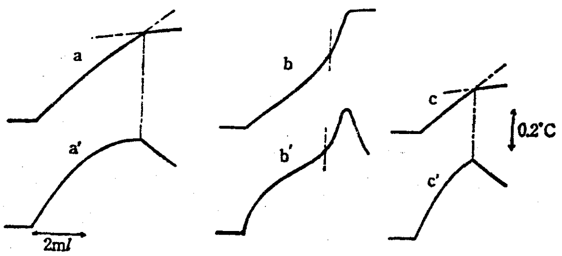


Fig. 4 Thermometric titration curves of amine mixtures in methyl cellosolve with hydrochloric acid standard solution.
(a,b,c; reference method, a',b',c'; differential method)
Amine mixture: similar as Fig.3.
a,a'; for the total amines, b,b'; for the secondary plus the tertiary amines, c,c'; for the tertiary amine.

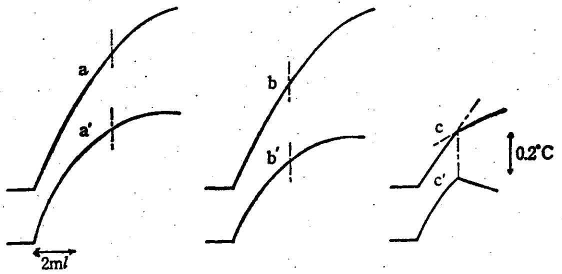


Fig. 5 Thermometric titration curves of amine mixtures in IPA with hydrochloric acid standard solution.
(a,b,c; reference method, a',b',c'; differential method)
a,a'; for the total amines, b,b'; for the secondard plus the tertiary amines, c,c'; for the tertiary amine.

Titration curves for amine mixtures with perchloric acid.

Mixtures of α-naphthylamine, N-methyl-α-naphthylamine, and N,N-dimethyl-α-naphthylamine were prepared as described in *Sample solution* for respective purposes of determinations, and titrated with standard perchloric acid in dioxane. Titration curves are shown in Fig.6. Similar titration curves were also obtained for the titrations in MIBK, acetonitrile, or glacial acetic acid. Titration curves obtained in methyl cellosolve are shown in Fig.7 and those in IPA in Fig.8. Simillar titration curves were also obtained in G-H solvent. From these Figs. the facts were recognized as follows.

(1) Titration curves for tertiary amine in MIBK, acetonitrile or glacial acetic acid(Fig.6) asended steeply after its inflection corresponding to the equivalence point of the tertiary amine, because of the reaction heat evolved by acid-catalyzed hydrolysis of acetic anhydride. Therefore, the second inflection corresponding amines did not appear. From this fact the acid-catalyzed hydrolysis was found to be unuseful for the end point indication of weakly basic substances such as aromatic amines, despite this reaction was very useful for the end point of amides of aliphatic amines.

(2) In methyl cellosolve(Fig.7) and in G-H solvent titration curves for secondary plus tertiary amines showed

their inflection corresponding to the sum of the two amines, and then ascended steeply, as shown in Fig.7b,b', because of the heat of acid-catalyzed acetal-formating reaction of salicylaldehyde. This phenomena were different from the cases, as shown in Fig4b,b', where hydrochloric acid was used as a titrant. Similar sharp inflections could be observed in the titration of a mixture of aniline, N-methylaniline, N,N-dimethylaniline. From the above facts, perchloric acid seemed to be superior to hydrochloric acid when the titration was carried out in methyl cellosolve or G-H solvent.

(3) In IPA the titration curves for total amines and those for secondary plus tertiary amines showed their remarkable inflections as shown in Fig.8. Compared with the case of hydrochloric acid, it is apparent that perchloric acid is a solvent superior to hydrochloric acid also in IPA.

It was clarified that when perchloric acid was used a standard titrant solution IPA, methyl cellosolve, and G-H solvent should be preferred out of seven solvent examined to obtain good results.

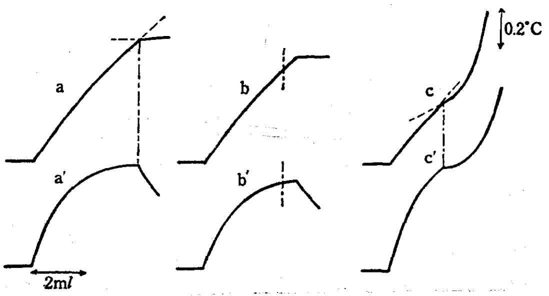


Fig. 6 Thermometric titration curves of amine mixtures in dioxane with perchloric acid standard solution.
(a,b,c; reference method, a', b',c'; differential method)
Amine mixture: 0.01M α-naphthylamine+0.01M N-methyl-α-naphthylamine +0.02M N,N-dimethyl-α-naphtylamine.
a,a'; for the total amines, b,b'; for the secondary plus the tertiary amines, c,c'; for the tertiary amine.

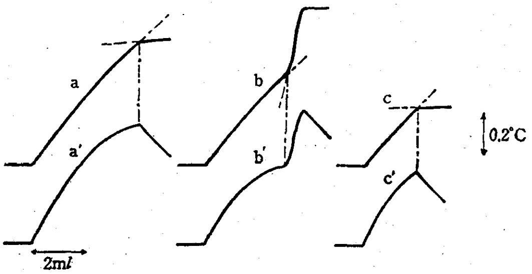


Fig. 7 Thermometric titration curves of amine mixtures in methyl cellosolve with perchloric acid standard solution.
Amine mixture, a,a',b,b',c, and c' are similar as Fig.6.

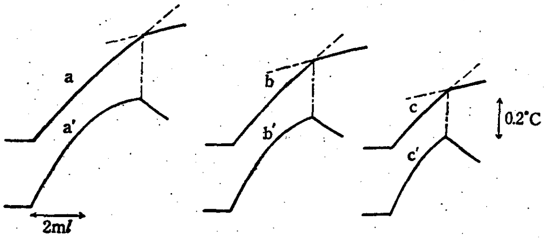


Fig. 8 Thermometric titration curves of amine mixtures in IPA with perchloric acid standard solution.
Amine mixture, a,a',b,b',c, and c' are similar as Fig.6.

Table 3 Precision and accuracy obtained in the titrations of pre-treated amine mixture with perchloric acid standard solution.

		Total amine*		Primary amine**		Secod. amine**		Secon+ tert. amine*		Tertiary amine*	
Amine mixture	Solvent	Preci. (%)	Accur. (%)	Preci. (%)	Accur. (%)	Preci. (%)	Accur. (%)	Preci. (%)	Accur. (%)	Preci. (%)	Accur. (%)
Aniline	IPA	0.5_3	0.6_6	0.6_9	0.8_5	0.6_3	0.7_9	0.6_6	0.7_8	0.4_4	0.4_8
N-methyl-aniline	G-H solvent	0.5_5	0.6_8	0.6_1	0.8_0	0.5_2	0.6_0	0.6_0	0.6_1	0.4_0	0.4_5
N,N-dimethyl-aniline	Methyl cellosolve	0.5_0	0.6_6	0.6_6	0.7_7	0.5_8	0.6_0	0.5_8	0.6_1	0.4_1	0.4_1
α-Naphthylamine	IPA	0.5_8	0.5_8	0.6_7	0.9_0	0.6_2	0.8_0	0.6_9	0.8_1	0.4_2	0.4_8
N-dimethyl-α-naphthylamine	G-H solvent	0.5_2	0.6_0	0.5_8	0.8_7	0.5_0	0.6_0	0.5_5	0.6_0	0.4_0	0.4_1
N,N-dimethyl-α-naphthylamine	Methyl cellosolve	0.5_1	0.6_0	0.6_0	0.7_9	0.6_0	0.6_8	0.5_0	0.5_8	0.4_3	0.4_8

* Values read directly from the titration curve.

** Values of primary amine obtained by subtracting the secondary plus tertiary amines from the total amine and values of secondary amine obtained by subtracting the tertiary amine from the secondary plus tertiary amines.

Quantitative results for amine mixtures

Based on the above results mixture of aniline, N-methylaniline and N,N-dimethylaniline and that of α-naphthylamine, N-methyl-α-naphthylamine and N,N-dimethyl-α-naphthylamine were titrated with standard perchloric acid solution in IPA, G-H solvent, and methyl cellosolve. As shown in Table 3, total amounts of amines, the sum of primary and tertiary amines and the amount of tertiary amine were respectively determined with satisfactry precision and accuracy only by reading the consumed volume of the acid from the titration curves. The amount of individual amines could be calculated by deducting the above measured amounts from each other.

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