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DETERMINATION OF AMMONIA, AMIDES, AND THE DEGREE OF HYDROLYSIS OF PARTIALLY HYDROLYZED POLYACRYLAMIDE BY THERMOMETRIC TITRATION AND DIRECT INJECTION ENTHALPIMETRY

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ABSTRACT

The properties of partially hydrolyzed polyacrylamide (PHPA) solutions are influenced by the degree of hydrolysis of the amide function. Solutions of PHPA usually contain ammonia and strong base left from the preparative hydrolysis reaction. Methods for determining the carboxyl function and ammonia by a thermometric titration with HCl, and the amide function by direct injection enthalpimetry with hypobromite are described in this paper. The data from both determinations on a given sample are combined to correct for interferences from ammonia in the amide determination and to make it unnecessary to know the total amount of polymer present in order to calculate the degree of hydrolysis. The determination with hypobromite is generally applicable to ammonia, amides which will undergo the Hoffman degradation reaction, and amines which can be oxidized by hypobromite. The detection limit is about 0.1 mM in all cases.

INTRODUCTION

Polyacrylamide (PAA) and partially hydrolyzed polyacrylamide (PHPA) are commonly used as viscosifiers, thickeners, and flocculants in aqueous solutions. Some of the common applications are in petroleum recovery and sewage treatment. The properties of the polymer depend on the degree to which the amide groups have been converted to carboxyl groups by hydrolysis. A rapid, simple method for determining the degree of hydrolysis has application to several areas of industrial chemistry.

PHPA is typically available as a solution in water prepared by polymerization of acrylamide followed by partial hydrolysis with strong base and heat. The degree of hydrolysis is usually controlled by the amount of base added. The concentration of polymer in the final solution is usually only roughly known. Thus, the method of analysis must be applicable to aqueous solutions and must either be independent of or determine the total polymer concentration.

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Previous methods for determining amide and carboxyl groups in polymers are either time consuming or only applicable to a narrow range of conditons. A recent report [1] describes the determination of the composition of acrylamide/acrylate copolymers by thermogravimetry (TG), but the method depends on being able to precipitate the polymer with alcohol, a procedure which does not work with some polymer preparations. Also, although the authors do not mention it, the method as described is applicable only to the sodium salt since other salts will produce a different TG curve. Infrared spectrophotometry, which has been used to determine carboxyl and amide groups in polymers [2,3] is not applicable to aqueous solutions although a film can sometimes be cast for analysis. The reactions normally used to determine amides cannot be used with PHPA because PHPA is not soluble in organic solvents and water interferes with the reactions [4]. Determination of total nitrogen as ammonia requires lengthy reaction times at high temperatures to hydrolyze the polymer completely [4], and residual ammonia must be removed before the analysis can be done accurately. Also, any method requiring the separation of solids cannot be used because of the viscosity of PHPA solutions. The ammonia present in PHPA solutions from the PAA hydrolysis interferes with the amperometric titration of amides with calcium hypochlorite [4,5]. Although this interference could be overcome in the same way we eventually chose to correct for the interference of ammonia in the amide determination, the amperometric method would require the use of an additional instrument.

The purpose of this paper is to report a thermometric titration method for the determination of carboxyl groups and a direct injection enthalpimetric method for the determination of amide groups in water soluble polymers. The two determinations require the same equipment, and when done on the same sample provide all of the necessary information to calculate the degree of hydrolysis. The method developed here for the determination of amides can be generally applied to any water soluble amide, ammonia, and oxidizable ammines. The detection limit is about 0.1 mM.

EXPERIMENTAL

Reagents

Standard 0.4 M HCl, 2 M NaCl, and neat *o*-bromoaniline are required for the thermometric titration of carboxyl groups in PHPA. For the determination of amide groups, 3 M NaOH, bromine, and standard solutions of ammonium chloride and unhydrolyzed polyacrylamide (0.01 to 0.05% in 1 M NaCl) are also required. In this study reagent grade chemicals were used except for *o*-bromoaniline (Eastman) and PAA standards (prepared from weight from a standard concentrate supplied by Marathon Oil Co.). The samples of PHPA were also supplied by Marathon Oil Co. as concentrated aqueous solutions of known concentration.

Equipment

A Tronac model 450 isoperibol titration calorimeter [6] equipped with a 25 ml Dewar, a 10 ml motorized buret delivering 0.05 ml min^{-1}, and a Hewlett-Packard recorder model 7100B was used to collect the thermometric titration and direct injection enthalpimetric data in this report. The water bath of the calorimeter was controlled at 298 K. The thermistor bridge had a sensitivity of about 20 mV K^{-1} and the thermal equivalent of the calorimeter was 4.90 ± 0.04 J mV^{-1}. Because of the viscosity of the solutions, the thin-bladed stirrer normally supplied with the calorimeter did not give adequate mixing and was replaced with a stirrer with hemispherical, 45° angled blades. The stirrer was driven at 800 rpm in the direction of rotation so as to push down on the solution. If the stirrer is driven in the normal direction, i.e. so that it lifts the solution, the polymer tends to wind onto the stirrer shaft and rise into the bearing.

For the thermometric titrations the recorder was operated at 0.5 mV full scale and 6 inch/min chart speed. For the direct injection enthalpimetric determinations the recorder was operated at 1, 5, or 10 mV full scale as appropriate and at 0.5 inch/min.

Thermometric titration procedure

The PHPA solution was diluted with water and 2 M NaCl so that the final concentration of PHPA was less than 0.07% and the NaCl was 1 M; 20 to 22 g of this solution was weighed into the Dewar, 0.3 ml of *o*-bromoaniline was added to the Dewar, the Dewar was placed on the calorimeter and the titration was done in the usual fashion. Figure 1 shows the form of the thermogram and the method of data analysis.

Direct injection enthalpimetry procedure

The titrant was prepared by dissolving 6 g of bromine in 35 ml of 3 M NaOH. This solution must be protected from the atmosphere and light by storage in an opaque, sealed, plastic container and must be prepared fresh weekly. The PHPA solution was diluted with water, 2 M NaCl, and 3 M NaOH so that the final solution is 1 M NaCl, 1 M NaOH and less than 0.05% PHPA. (This solution can conveniently be prepared from the solution used for the thermometric titration by mixing that solution with 3 M NaOH and 2 M NaCl in a 1 : 1 : 1 volume ratio.) Then 20 to 22 g of this solution was weighed into the Dewar, the Dewar was placed on the calorimeter, the temperature was brought to bath temperature, and 0.35 ml of titrant was

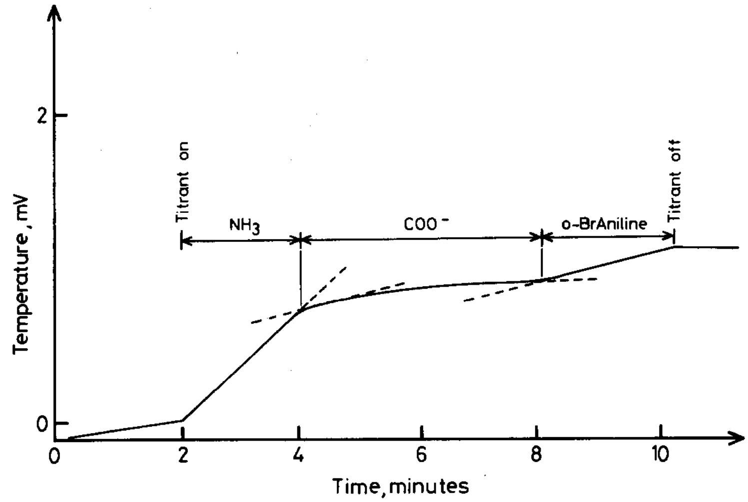

Fig. 1. Schematic drawing of the thermogram obtained by titration of PHPA solutions with strong acid.

injected with the buret (0.05 ml min^{-1}). The chart was allowed to run until a straight line with a slope less than the lead was obtained. A blank was determined for each determination by cooling the Dewar back below bath temperature and repeating the injection of hypobromite. The purpose of the blank was to correct for any acid–base, halogen exchange, or dilution reactions which may have occurred. The blank was always found to be small for the solutions used here. Figure 2 shows the form of the data obtained

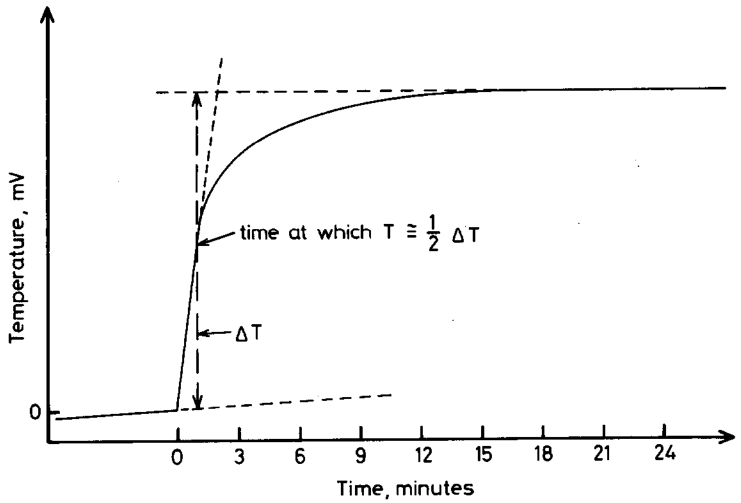

Fig. 2. Schematic drawing of the thermogram obtained by injection of hypobromite solution into PHPA solution.

and the method of data analysis. If ammonia or oxidizable amines are present as shown by the thermometric titration, the measured temperature rise must be corrected for the heat of reaction of these compounds with hypobromite. Other reducing agents and monomeric amides which are not determined by the thermometric titration will also interfere in the amide determination and must be determined independently and corrected for if present.

RESULTS

Figure 3 shows the data obtained on ammonia and two monomeric amides. Ammonia was the only interferent present in the PHPA solutions used in this study. The data on the amides was obtained to see if the enthalpy change for the hypobromite reaction was dependent on the molecular structure. It was originally hoped that a single calibration constant could

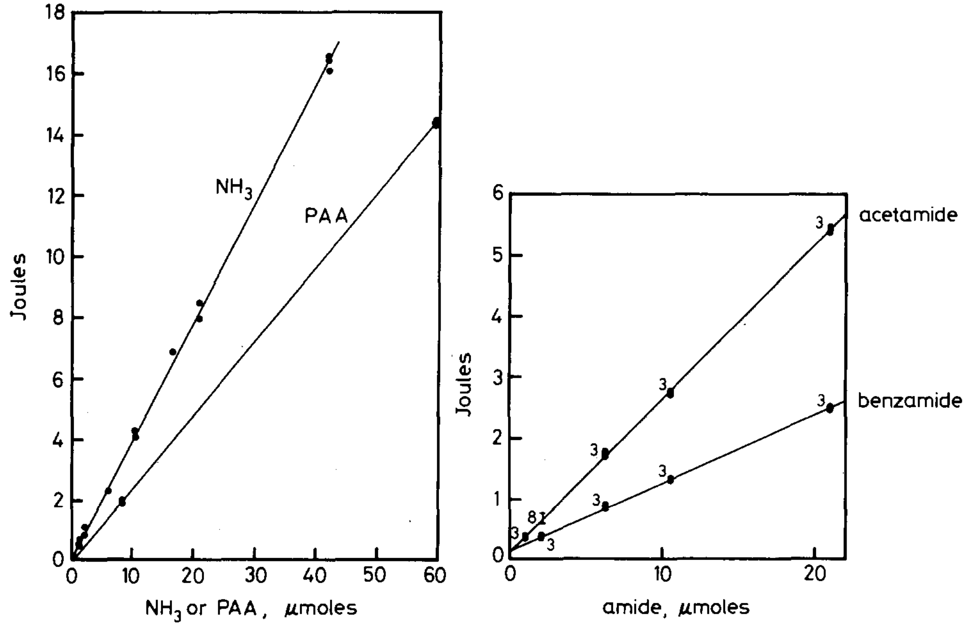

Fig. 3. Heat produced in the reaction of excess hypobromite with ammonia, acetamide, benzamide, and PAA as a function of the concentration or amount of ammonia or amide. The equations for the linear least square lines shown are Joules = $(0.08 \pm 0.06) + (0.392 \pm 0.003)\mu\text{mol}$ for ammonia, Joules = $(0.13 \pm 0.01) + (0.252 \pm 0.001)\mu\text{mol}$ for acetamide, Joules = $(0.15 \pm 0.01) + (0.112 \pm 0.001)\mu\text{mol}$ for benzamide, and Joules = $(-0.11 \pm 0.06) + (0.243 \pm 0.002)\mu\text{moles}$ for PAA. The numbers shown by the symbols in the figures indicate the number of determinations done at that point. The symbols show the spread of the data.

TABLE 1

Results of thermometric titrations of PHPA solutions

Solution[a]	PHPA taken (μmol of monomeric units[b])	NH_3 found (μmol)[c]	COO^- found (μmol)	%Hydrolyzed[d]
PAA	170	0±2[e]	0.0±0.8	0.0±0.5
10	174	12±2	32 ±2	19 ±1
30	188	34±3	50 ±3	27 ±2
50	202	65±3	68 ±5	34 ±3

[a] As identified by the nominal percent of amide groups hydrolyzed.

[b] A monomeric unit has a molecular weight of 71.

[c] From the thermograms, NH_3 and traces of OH^- and CO_3^{2-} were the only bases stronger than COO^- which were present. The ammonia was identified from the heat of the reaction.

[d] Based on the known concentration of PHPA.

[e] Error limits are given as the standard deviation of the mean of three or four determinations.

be used for all amides. As is obvious from the data in Fig. 3, a different calibration constant must be used for each different amide.

The thermometric titration results are given in Table 1, the direct injec-

TABLE 2

Results of determination of amide groups in PHPA

Solution[a]	PHPA taken (μmol of monomeric units[b])	NH_3 taken (μmol[c])	ΔT calculated for NH_3[d]	ΔT measured (mV)	Amide found (μmol[e])	%Hydrolyzed[f]
PAA	59.6	0	0	2.94±0.01[g]		(0.0493 mV μmol^{-1})
	8.50	0	0	0.40±0.01[g]		(0.0471 mV μmol^{-1})
					Average:	0.0482±0.0015
10	60.8	4.19	0.33	2.87	52.7	13.3
	8.69	0.60	0.05	0.37	7.3	16
					Average:	15 ±2
30	65.8	11.97	0.96	3.49	52.5	20.2
	9.40	1.71	0.14	0.47	6.8	28
					Average:	24 ±6
50	70.8	22.64	1.82	3.96	44.4	37.3
	10.1	1.84	0.15	0.49	7.1	30
					Average:	34 ±5

[a] Solutions are identified by the nominal percentage of amide groups hydrolyzed.

[b] A monomeric unit has a molecular weight of 71.

[c] Calculated from data in Table 1.

[d] Equal to $0.0803 \times \mu$mol NH_3. See Fig. 1.

[e] Equal to $(\Delta T \text{ measured} - \Delta T_{NH_3})/0.0482$.

[f] Based on the known concentration of PHPA.

[g] Standard deviation of the mean of triplicate determinations.

TABLE 3

Comparison of the percentage of amide groups hydrolyzed as determined by different methods

Solution [a]	%Hydrolyzed by thermometric titrimetry and PHPA	%Hydrolyzed by DIE with hypobromite and PHPA	%Hydrolyzed by thermometric titrimetry and DIE with hypobromite
10	19 ± 1	15 ± 2	18 ± 1
30	27 ± 2	24 ± 6	26 ± 2
50	34 ± 3	34 ± 5	34 ± 3

[a] Solutions are identified by the nominal percentage of amide groups hydrolyzed.

TABLE 4

Determination of amide groups in PHPA solutions made 1 M in NaOH and argon purged for 24 h

Solution [a]	PHPA taken (monomeric units) [b]	ΔT measured (mV)	Amide found (μmol)	%Hydrolyzed
10	60.8	1.52 ± 0.07 [c]	31.5 ± 1.5	52 ± 2
30	65.8	1.74 ± 0.00	36.1 ± 0.0	55 ± 0
50	70.8	1.67 ± 0.05	34.6 ± 1.0	49 ± 1

[a] Solutions are identified by the nominal percentage of amide groups hydrolyzed. After treatment with NaOH and Ar, these solutions were free from ammonia as indicated by the indophenol spot test.

[b] A monomeric unit has a molecular weight of 71.

[c] Error limits are the standard deviation of two determinations.

tion enthalpimetry results are given in Table 2, and a comparison of these results and the results derived from a combination of the methods is given in Table 3. Since ammonia interferes in the determination of the amide groups with hypobromite [5], an attempt was made to remove the ammonia by making the PHPA solution basic with NaOH and purging the solution with argon at room temperature. Even this mild treatment was found to result in 50% hydrolysis of the amide groups as shown in Table 4.

DISCUSSION

The data in Fig. 3 show that the direct injection enthalpimetric method described here can be used to determine a wide range of amides and amines. The data in Table 1 show that thermometric titration with strong acid in water can be used successfully to titrate carboxyl groups in polymers using a thermochemical indicator. The data in Table 3 show that all three methods are in agreement.

The results shown in Table 4 are of interest mainly because they show that the first half of the amide groups in PAA are rather easily hydrolyzed. This caused us some concern about the stability of the solutions used as standards in this work. However, no detectable change in the degree of hydrolysis was found over the one month period during which data were collected.

Some of the conditions chosen for the determinations described in this paper require further explanation. The PAA and PHPA samples used had molecular weights of 7 to 9 million, and, as a result, the viscosity of even the dilute solutions used in the procedures was quite high. The viscosity determined the maximum concentrations of PHPA which could be used. The determinations were all done in 1 M salt solutions in order further to reduce the viscosity. The very high molecular weight also meant that the polymers could not be precipitated from solution by the addition of organic solvents, nor could the solutions be filtered. Treatment of the polymer solutions with organic solvents resulted in the formation of sticky lumps of thick gel which were impossible to treat in any quantitative fashion. The only successful way to remove the water from the PHPA that we could find was freeze drying, but the IR spectra of the freeze dried products from the solutions always indicated the presence of residual water even after an extended time under vacuum.

An attempt was made to determine the carboxyl group by pH titration, but it was found that the apparent pK_a value varied continuously from about 7 to less than 2 so that no useful endpoint could by found. The use of a thermochemical indicator [7], *o*-bromoaniline, in a thermometric titration was used to solve this problem. The use of an insoluble indicator results in a straight line in the thermogram after the endpoint because the indicator dissolves as it reacts to form an ion. Because of the dissolution reaction, there is essentially the same amount of reaction with each increment of titrant and a linear rate of heat production results. The titration of such a weak base would result in a curved thermogram if the base were soluble. For example, the use of sulfate as a thermochemical indicator [7] did not work in this case because of the curvature of the thermogram during the titration of sulfate with acid. The titration curve for the carboxyl groups is slightly curved because the reaction becomes more endothermic with the degree of protonation of the carboxyl groups. (This change in the heat of protonation may be due to the initial stages of precipitation of the polymer, but no visible precipitate or cloudiness was observed in the solutions used in this study.) Since the protonation of sulfate is also endothermic the two curves simply overlapped to produce a curve with no definitive or reproducible endpoint. It became apparent that what was needed was a base with an exothermic heat of protonation and a pK_a near 2. *o*-Bromoaniline with a pK_a of about 2.5 and a heat of protonation of about -20 kJ mol^{-1} was available and was found to give a good endpoint. Other substituted anilines would probably work equally well. The very low water solubility of *o*-bromoaniline proved to be a useful property resulting in the thermogram after the endpoint being a straight line because of the excess reagent present in a second phase.

A slow delivery rate of titrant and special efforts to obtain rapid mixing were found to be necessary to obtain reproducible results in both the thermometric titration and the direct injection enthalpimetry. A faster delivery rate resulted in increased noise in the titration curve and in irreproducible results in the injection. There apparently are reactions other than the Hoffman degradation which can take place if a local excess of hypobromite is present.

The hypobromite reaction was found to be too slow and too incomplete to be run in less basic solutions than the 1 M NaOH used here.

In conclusion, the methods described here use simple, inexpensive, commercially available equipment and are applicable to a wide range of commercially important materials.

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