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Protonation of Polyethylenimine

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NOTE

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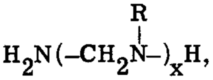
Protonation of polyethylenimine (PEI) has been studied by various investigators [1-4]. Most studies involved potentiometric titrations with hydrochloric acid and the effect of added salts. Liu [5] has reported the specific influence of chloride, bromide, and nitrate ions on the viscosity of solutions of protonated PEI. It has been noticed that, when a small amount of PEI is added to ammonium nitrate, gaseous ammonia is produced. No information, however, has been found concerning the quantitative basis of the reaction. The study of the quantitative nature of protonated PEI by various reagents is reported in this note. In general, agreement with previous work is excellent. It also shows slight variation on the degree of protonation by various reagents.

The general structure of PEI (Corcat P-150, Cordova Chemical Co., MW 10 000) is



$$H_2N(-CH_2\overset{R}{\overset{|}{N}}-)_xH,$$

where $R = (-CH_2CH_2\overset{R}{\overset{|}{N}}-)_yH$. According to the manufacturer, the PEI

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in Corcat P-150 consists of approximately 30% primary, 40% secondary, and 30% tertiary amines, and models indicate that the molecules are spheroid in nature. The distribution of primary, secondary, and tertiary amines in PEI will depend slightly upon the method of synthesis [3, 6]. The pH value of the P-150 solution is between 10 and 11, and the specific gravity is 1.04-1.06 at 25°C.

Protonation of PEI with Excess NH_4NO_3. Ammonia gas is given off upon direct addition of PEI to ammonium nitrate according to

$$\mathrm{PEI} + n\mathrm{NH_4NO_3} \longrightarrow \mathrm{PEI\cdot(HNO_3)_n} + n\mathrm{NH_3}.$$

The product, $\mathrm{PEI\cdot(HNO_3)_n}$, is a polyprotonated PEI nitrate salt and is here called PNEI for simplicity. The liberated ammonia gas is trapped in a known amount of standardized sulfuric acid. The excess sulfuric acid is then titrated with standardized sodium hydroxide solution. The amount of the ammonia produced, and thus the number of protons transferred to PEI, is determined by difference. Since one monomer unit of PEI is about 43 in MW and contains one amine functional group, one molecule of PEI, with a mass of 10 000, has approximately 232 amine sites. Thus, the percentage of the amine sites protonated can be calculated from the ammonia produced.

Protonation of PEI with Excess Ethylenediammonium Dinitrate (EDD).

$$\mathrm{PEI} + m\mathrm{EDD} \longrightarrow \mathrm{PEI\cdot(HNO_3)_{2m}} + m\mathrm{ED}.$$

The ethylenediamine (ED) formed in the above reaction is titrated with standardized acid to the methyl red end point. Monomer amines and low molecular weight PEI have pK values [3] at 10-11 and 7.5-9.5, respectively, and have their concentrations around 10^{-2} and 10^{-4} M, respectively. The pH at the neutralization point is expected to be about 5.5-6.5. Therefore, methyl red indicator is a reasonable choice for the titration. Both ED and EDD are bifunctional groups.

When PEI reacts with an excess of various acids, HNO_3, H_2SO_4, HCl, and $HClO_4$, the excess acids can be backtitrated with standard sodium hydroxide and the degree of protonation determined from the titer.

The protonation of PEI by various reagents shown in Table 1 indicates that approximately 70% of the total amine sites are protonated in PEI. There does seem to be, however, a very small variation in the percentage of amine sites protonated depending on the reagents used. In this study, the protonation of PEI was carried out to a high degree. Therefore, in general, the electrostatic repulsion of the polyion resulted in an expansion of the chain. It is therefore the open-

TABLE 1. Protonation of PEI By Various Reagents

Reagent	Weight of PEI, g	Reagent, meq	Protonation, %
NH_4NO_3	1.805	27.0	65
	2.781	43.9	68
EDD	0.761	6.2	70
	2.346	19.0	70
HNO_3	3.458	55.0	69
	3.492	55.5	69
H_2SO_4	4.290	71.5	72
	3.854	64.0	72
	3.716	61.5	71
HCl	3.132	49.8	69
	3.970	64.1	69
	2.310	36.5	68
$HClO_4$	3.191	48.2	65
	3.435	53.1	67

ness of the structure that accounts for the high percentage of protonation. The primary and secondary amine sites located near the spheroid surface are available for protonation as well as accessible to the solvent molecules. The tertiary amine sites are buried inside the PEI and are not easily titrated, probably because of hydrophobic interactions.

The stability of an expanded polyprotonated PEI will be enhanced if effective counterions exist. Sulfate and ethylenediamine dinitrate have two negative charges. They are more effective in stabilizing the polyprotonated PEI than monovalent chloride, nitrate, and perchlorate, while the latter is larger in size. Because of less stabilization of the protonated PEI by perchlorate ion, it can be interpreted, on the other hand, that protonated PEI with perchlorate counterions is more intramolecularly associated, probably due to hydrogen bonding. This seems to account for the small variation in protonation among the reagents used.

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