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Titration Curves of p-Aminobenzoic Acid-Formaldehyde-p-Bromoaniline Copolymers in Nonaqueous Media

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ABSTRACT

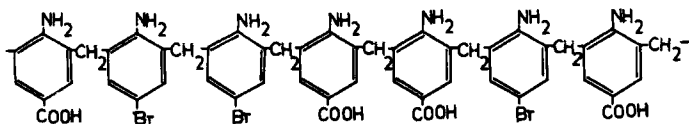
Copolymers obtained by condensation of p-aminobenzoic acid, p-bromoaniline, and formaldehyde in presence of acid catalyst have been separated into five fractions. Quantitative estimation of Br in each of the fractions was carried out, and the total amount of acidic and basic functional groups in given weight of the copolymer was calculated. Each of the fractions were titrated potentiometrically and conductometrically in nonaqueous solvents, and an excellent correlation was obtained for calculated and observed functional groups. The titration curves also indicated a series of breaks which bear an integral relation to each other. These features have been interpreted in terms of intramolecular hydrogen bonding, homoconjugation, and composition of the copolymers.

Preliminary work on some synthetic copolymers having acidic and basic functional groups revealed that the composition and structure of the copolymers could be correlated with their titration curves

in nonaqueous media [1, 2]. It was considered of interest to see whether titrimetric methods could be used to ascertain the DP and total acidity or basicity for a given weight of the copolymer. The copolymer obtained by condensation of p-aminobenzoic acid, formaldehyde, and p-bromoaniline was chosen for this investigation. This system is interesting in view of the fact that Br content of the fractions from the copolymer could be obtained by chemical analysis and each repeating unit of the copolymer contains an NH_2 group and a COOH or a Br group. Thus one can calculate, from the Br content of the various fractions, the mole ratio of p-aminobenzoic acid (PAB) and p-bromoaniline (PBA) in the copolymer chain; consequently the total acidity or basicity in a given weight of the copolymer could also be calculated. The titration curves in nonaqueous media of the various fractions of the copolymer showed some interesting features. First, an excellent correlation could be seen between the calculated quantity of total acidity/basicity and their observed values. Secondly, a number of additional inflections were observed before the complete neutralization of acidic/basic groups in a given weight of the copolymer. These breaks occur in multiples of a "smallest interval" of added base/acid, and this smallest interval was found to be different for the various fractions. An attempt has been made in this paper to correlate the hyperacid character of the functional groups with intramolecular hydrogen bonding and estimation of DP of various fractions separated from the copolymer.

EXPERIMENTAL

p-Aminobenzoic acid-formaldehyde-p-bromoaniline copolymer (I) was prepared by refluxing a mixture of p-bromoaniline (0.5 mole), p-aminobenzoic acid (0.5 mole), and formaldehyde (1.0 mole) in the



I

presence of 2 cc of 10 *N* HCl as catalyst for 2.5 hr at 130° C. The reaction mixture was then poured into ice-cold water and washed several times with water to remove unreacted monomers. The polymer yield was about 80%. The copolymer thus obtained was

then fractionated by dissolving about 7.0 g of the product in methanol, the higher molecular weight fraction being separated on addition of water as nonsolvent. Approximately 1.70, 1.10, 1.30, 1.60, and 1.30 g of the copolymer separated at five consecutive stages of precipitation. The Br contents of the conglomerate and of the five fractions were found by treating the copolymer with sodium metal, and the resultant sodium bromide was estimated by Volhard's method [3].

A Radiometer pH meter (model pHM26c) with a glass (G202B) electrode and a calomel (K-401) electrode as reference was used for pH titrations, and a Leeds & Northrup conductance bridge (4959) was used for conductometric titrations. The titrations were mostly performed at room temperature and 2-3 min time was allowed after each addition of titrant to obtain equilibrium readings. The titration vessel was stirred with a magnetic stirrer which was switched off during each measurement. The copolymer concentration used was about 1.5 g/liter, and the titrant was standardized daily. Pyridine and glacial acetic acid were used as media for titrations and sodium methoxide and perchloric acid as titrant base and acid, respectively. The reproducibility of each titration curve was checked and found to be within 2-3%.

RESULTS AND DISCUSSION

Figures 1-6 show the potentiometric and conductometric titration curves of the copolymer I and the five fractions separated from it. The titrations were carried out in pyridine, sodium methoxide and in some cases tetramethylammonium hydroxide (TMAH) being used as titrant bases. The conductometric titration curves with sodium methoxide as titrant base (curves B in Figs. 1-6) of the copolymer and the five fractions invariably showed a distinct final break, which represents the complete neutralization of total COOH groups in a given weight of the copolymer. Some coincidence could be observed when the same copolymer and their fractions were titrated conductometrically in the same solvent with TMAH as titrant base (e.g., curves A in Figs. 1-6). The corresponding potentiometric curves (curves C in Figs. 1-6) of the copolymers showed only one or two very sharp inflections. Interestingly enough, the breaks or inflections of a particular fraction occur in multiples of a smallest interval, and this smallest interval is found to be different for the various fractions. The coincidence between breaks and inflections obtained for a particular fraction referred to the smallest interval only and does not refer to the presence of an inflection for every break in its conductometric curve. Since, on the basis of Br

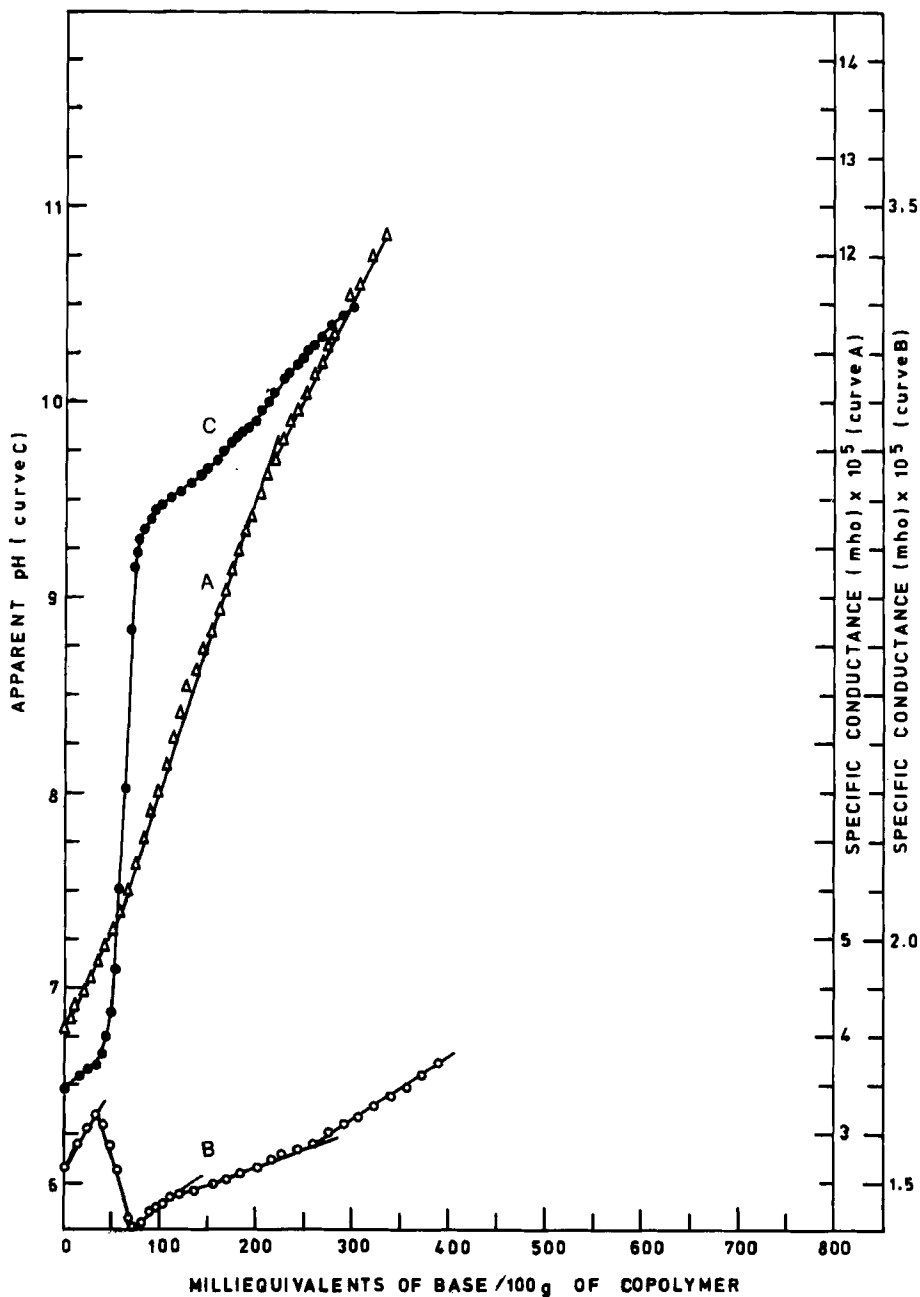


FIG. 1. Titration curves of conglomerate in pyridine: (A) conductometric curve, TMAH as titrant; (B) conductometric curve, sodium methoxide as titrant; (C) potentiometric curve, sodium methoxide as titrant.

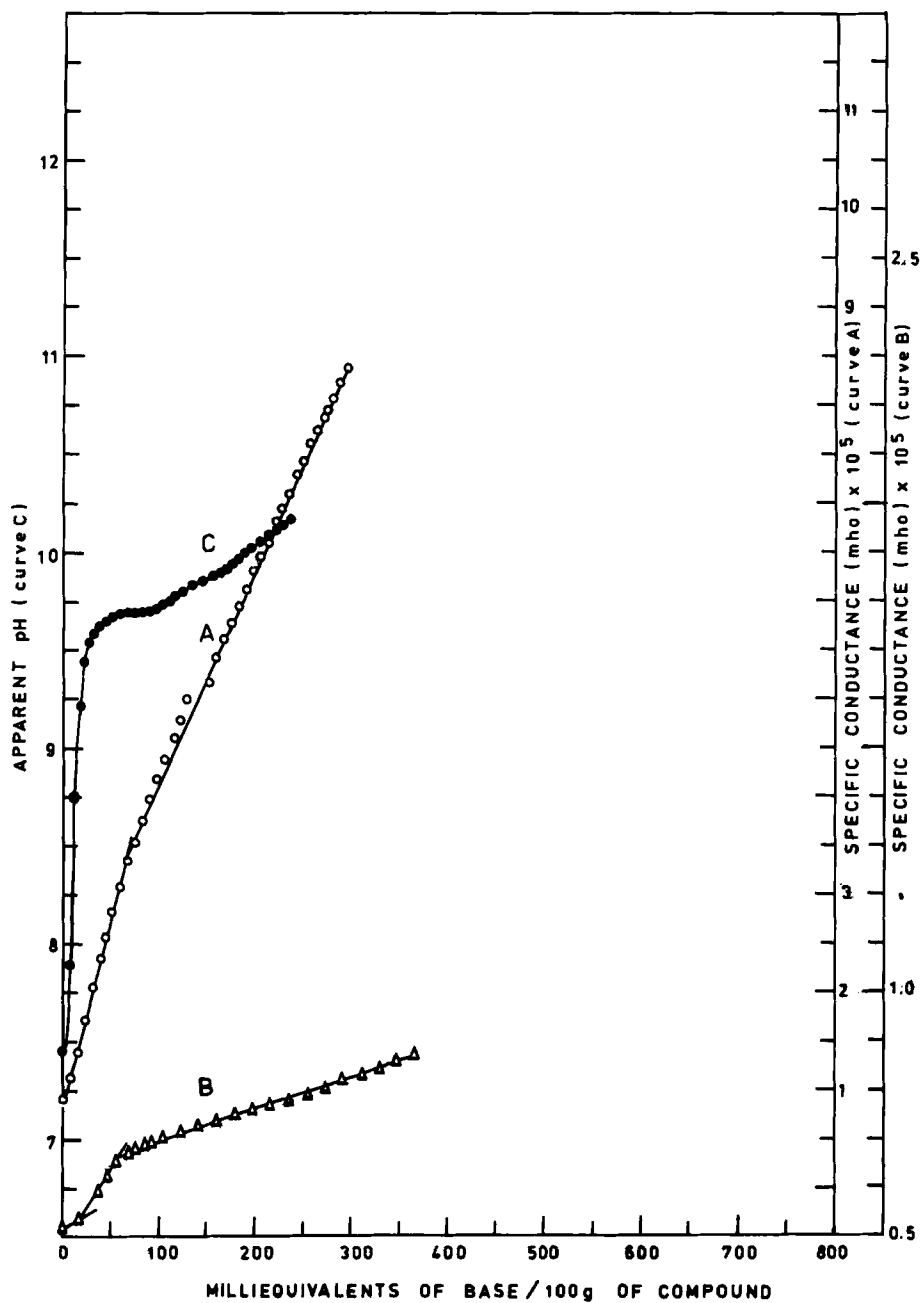


FIG. 2. Titration curves of fraction 1 in pyridine: (A) conductometric curve, TMAH as titrant; (B) conductometric curve, sodium methoxide as titrant; (C) potentiometric curve, sodium methoxide as titrant.

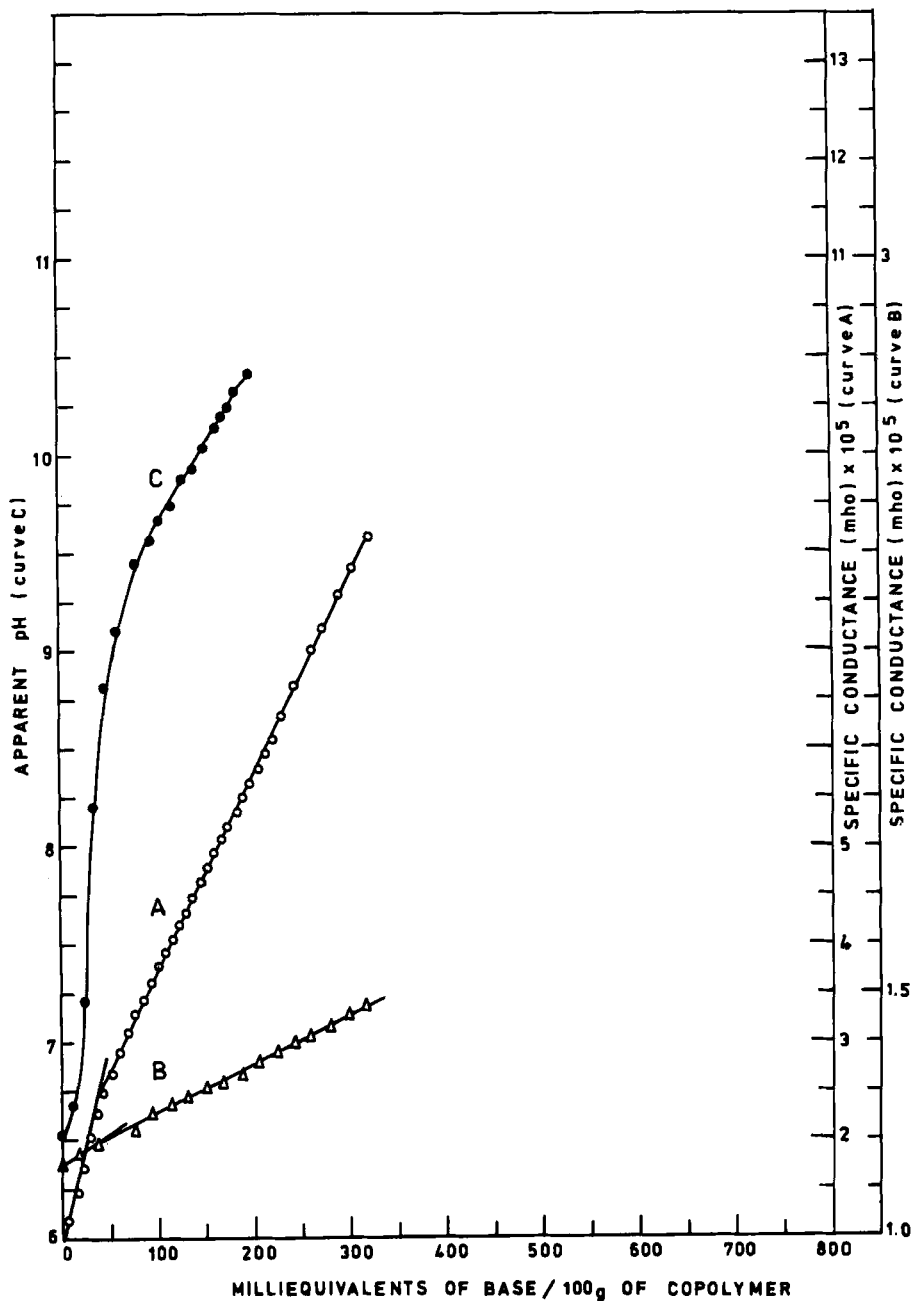


FIG. 3. Titration curves of fraction 2 in pyridine: (A) conductometric curve TMAH as titrant; (B) conductometric curves, sodium methoxide as titrant; (C) potentiometric curve, sodium methoxide as titrant.

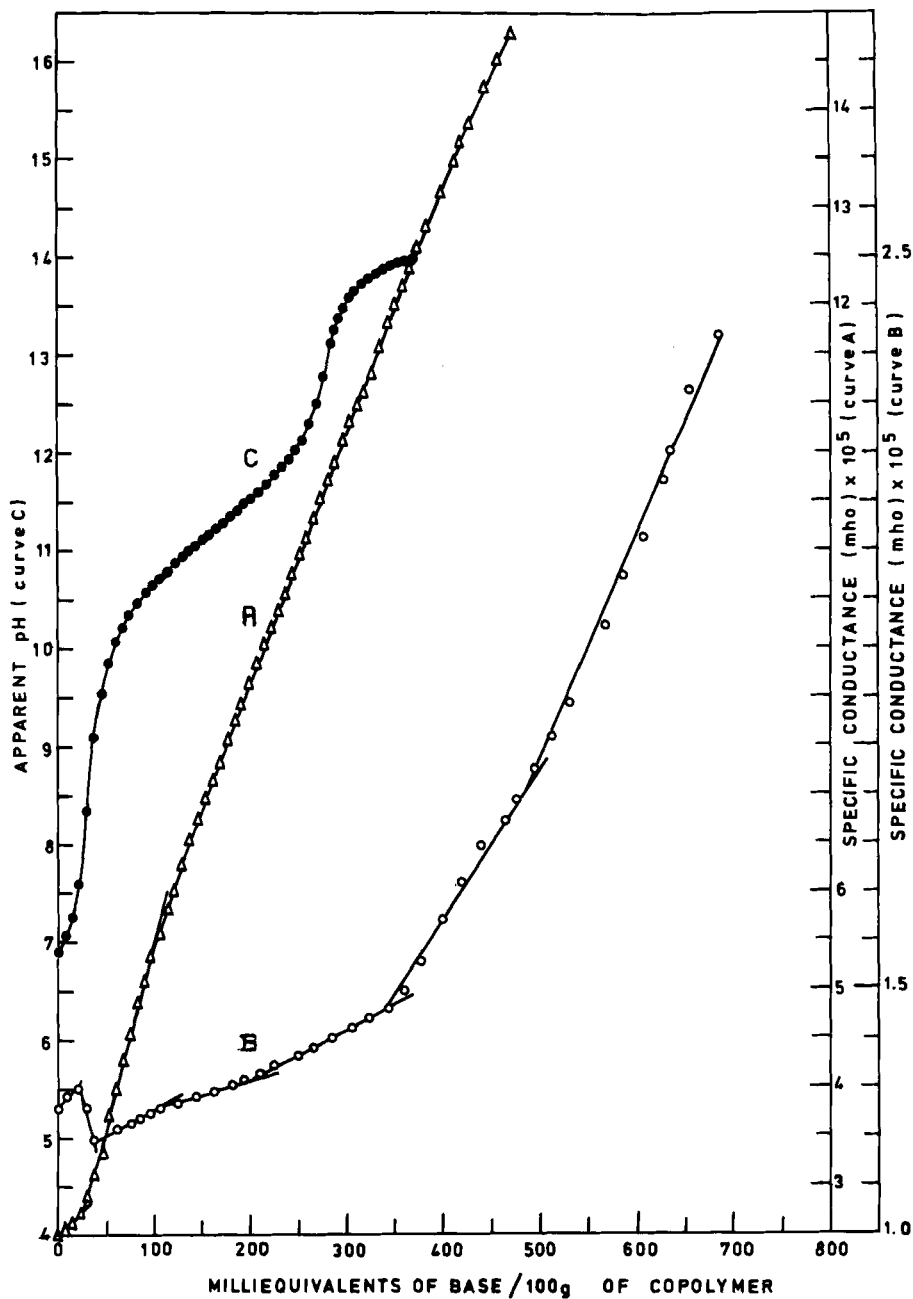


FIG. 4. Titration curves of fraction 3 in pyridine: (A) conductometric curve, TMAH as titrant; (B) conductometric curve, sodium methoxide as titrant; (C) potentiometric curve, sodium methoxide as titrant.

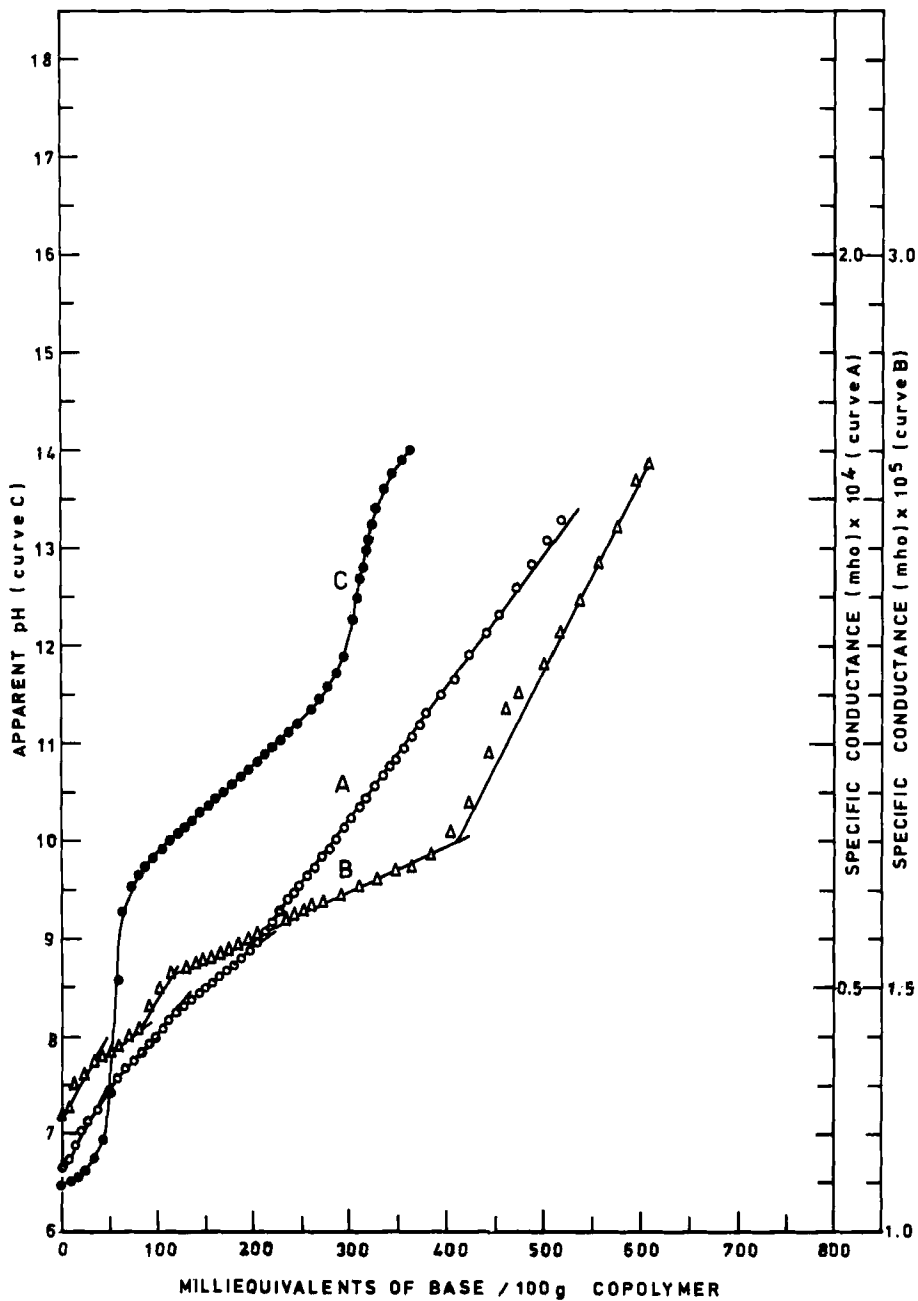


FIG. 5. Titration curves of fraction 4 in pyridine: (A) conductometric curve, TMAH as titrant; (B) conductometric curve, sodium methoxide as titrant; (C) potentiometric curve, sodium methoxide as titrant.

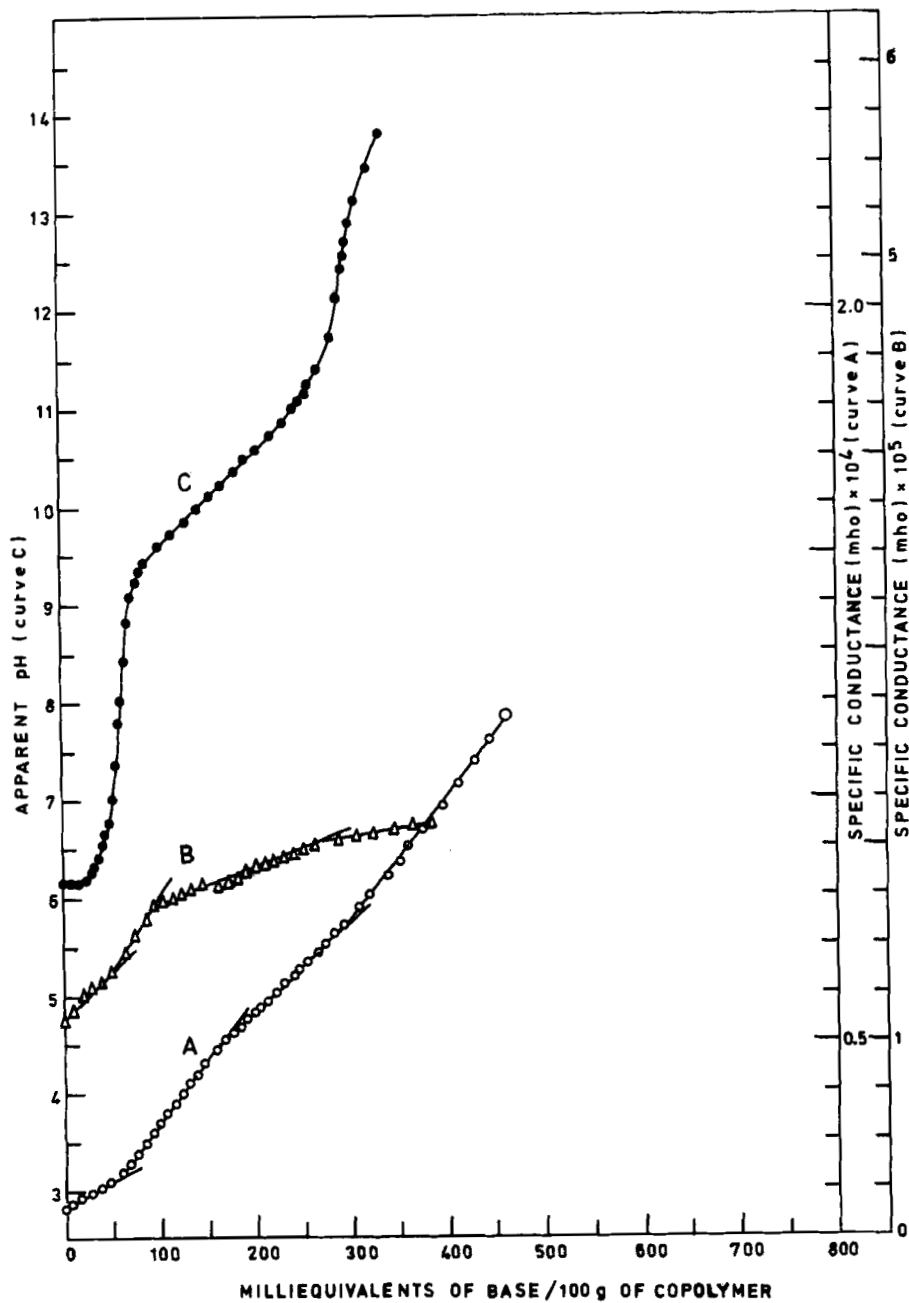
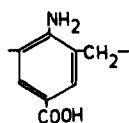
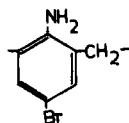


FIG. 6. Titration curves of fraction 5 in pyridine: (A) conductometric curve, TMAH as titrant; (B) conductometric curve, sodium methoxide as titrant; (C) potentiometric curve, sodium methoxide as titrant.

estimation of the conglomerate and of the various fractions, one can calculate the total amount of NH_2 and COOH groups in a given weight of the copolymer, it was considered worthwhile also to determine experimentally the total amount of NH_2 groups in a given weight of the conglomerate and the various fractions. Figures 7-12 show the conductometric and potentiometric curves of the conglomerate and the five fractions in glacial HAC medium with perchloric acid as titrant. The conductometric curves (curves A in Figs. 7-12) showed a number of breaks at definite intervals and the corresponding potentiometric curves (curves B in Figs. 7-12) showed invariably one sharp inflection. The smallest interval was found to be identical for a particular fraction, irrespective of whether it is titrated with base or an acid. The copolymer chains contain two distinct types of repeating units, which are either linked in a completely random manner, or there may be a small block of one type of repeating unit



A Unit



B Unit

followed by another block of the other repeating unit. Since both the repeating units A and B contain one equivalent each of NH_2 group and a COOH group or a Br group, on the basis of Br estimation of the conglomerate and each of the fractions, the total amount of NH_2 and COOH groups per 100/g of the copolymer can be calculated. Excellent agreement could be seen (Table 1) between the calculated total amount of NH_2 and COOH groups and the values found from the titration curves.

A distinct feature of the conductometric titration curves of the conglomerate and each of the fractions is the presence of a large number of additional breaks before the complete neutralization of acidic/basic functional groups in a given weight of the copolymer. As already mentioned, these breaks occur in multiples of a smallest interval between any two consecutive breaks. These observations are significant in view of the fact that each repeating unit of the copolymer contains an NH_2 group, and if we divide the calculated amount of acid required to neutralize all NH_2 groups in 100 g of copolymer by the amount required to neutralize one NH_2 group (smallest interval), the DP of copolymer can be calculated. The

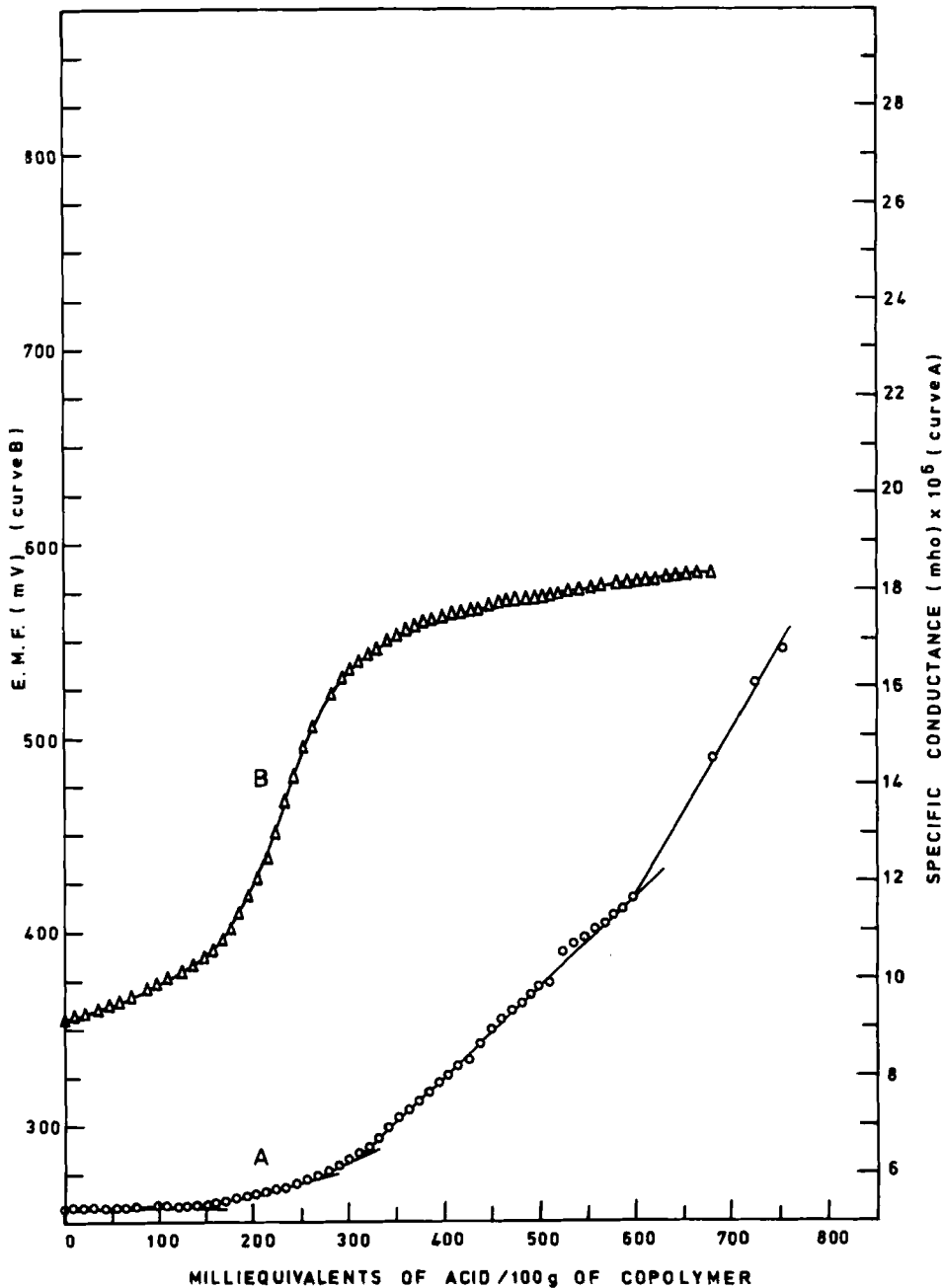


FIG. 7. Titration curves of conglomerate in glacial acetic acid with perchloric acid as titrant: (A) conductometric curve; (B) potentiometric curve.

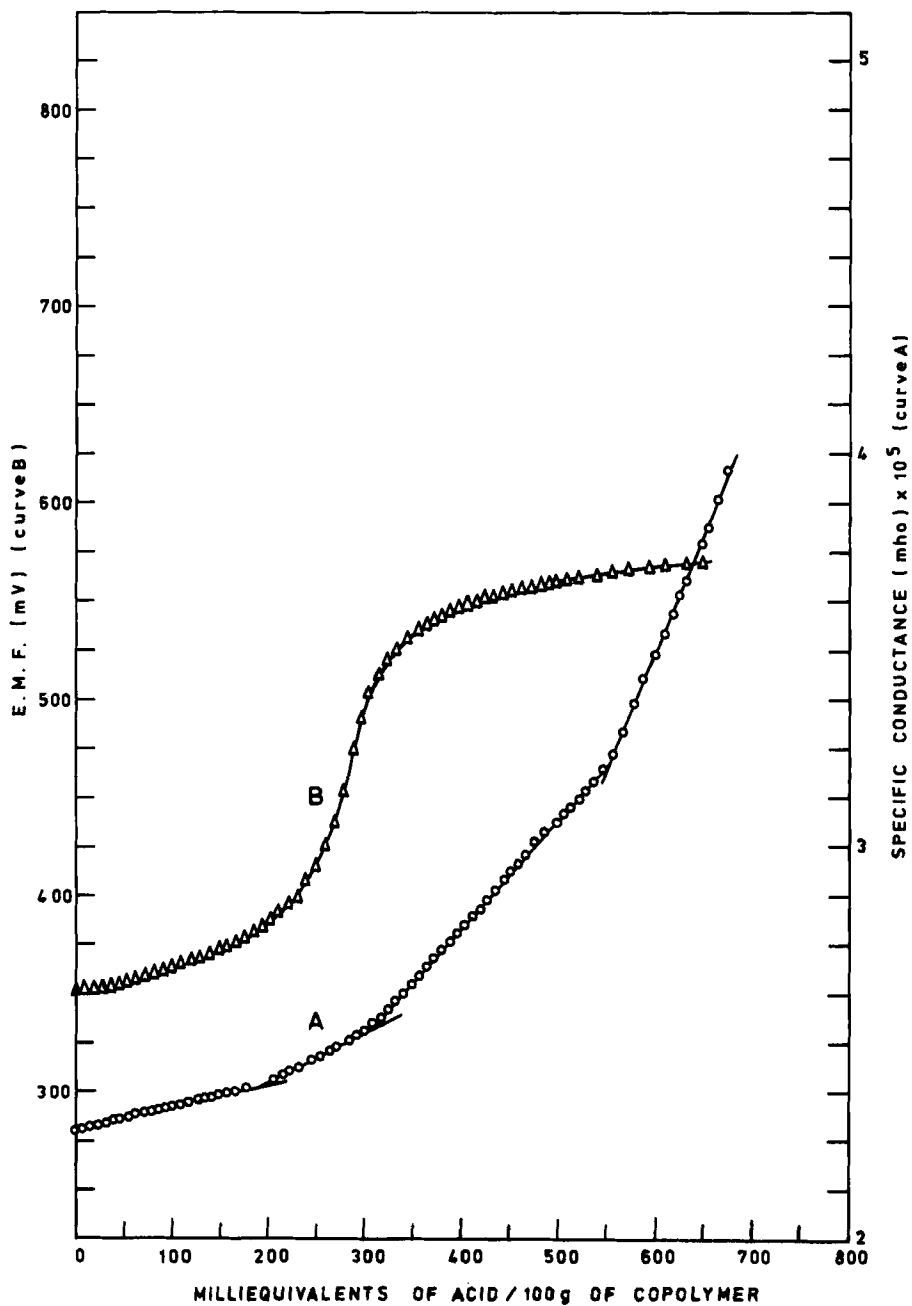


FIG. 8. Titration curves of fraction 1 in glacial acetic acid with perchloric acid as titrant: (A) conductometric curve; (B) potentiometric curve.

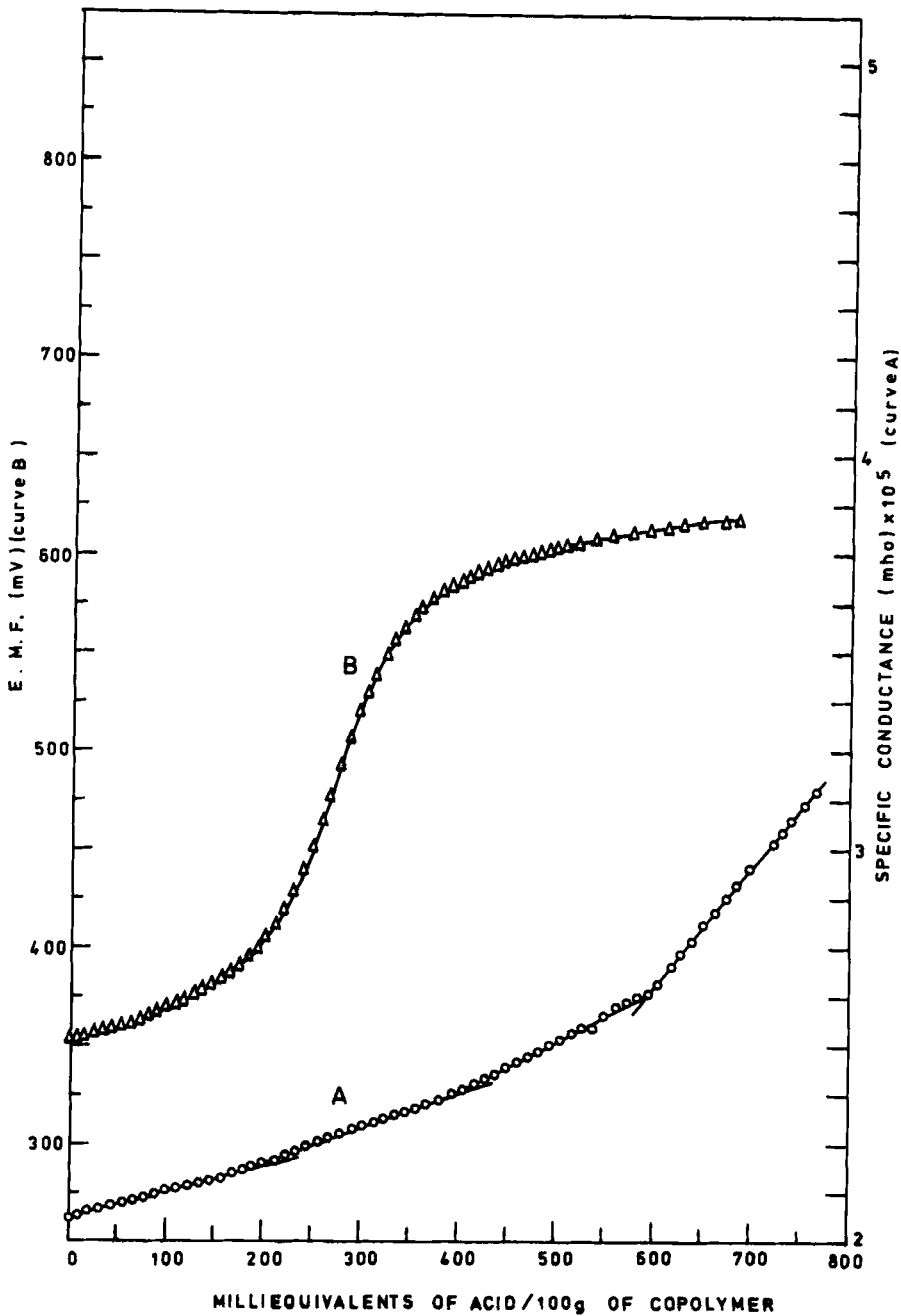


FIG. 9. Titration curves of fraction 2 in glacial acetic acid with perchloric acid as titrant: (A) conductometric curve; (B) potentiometric curve.

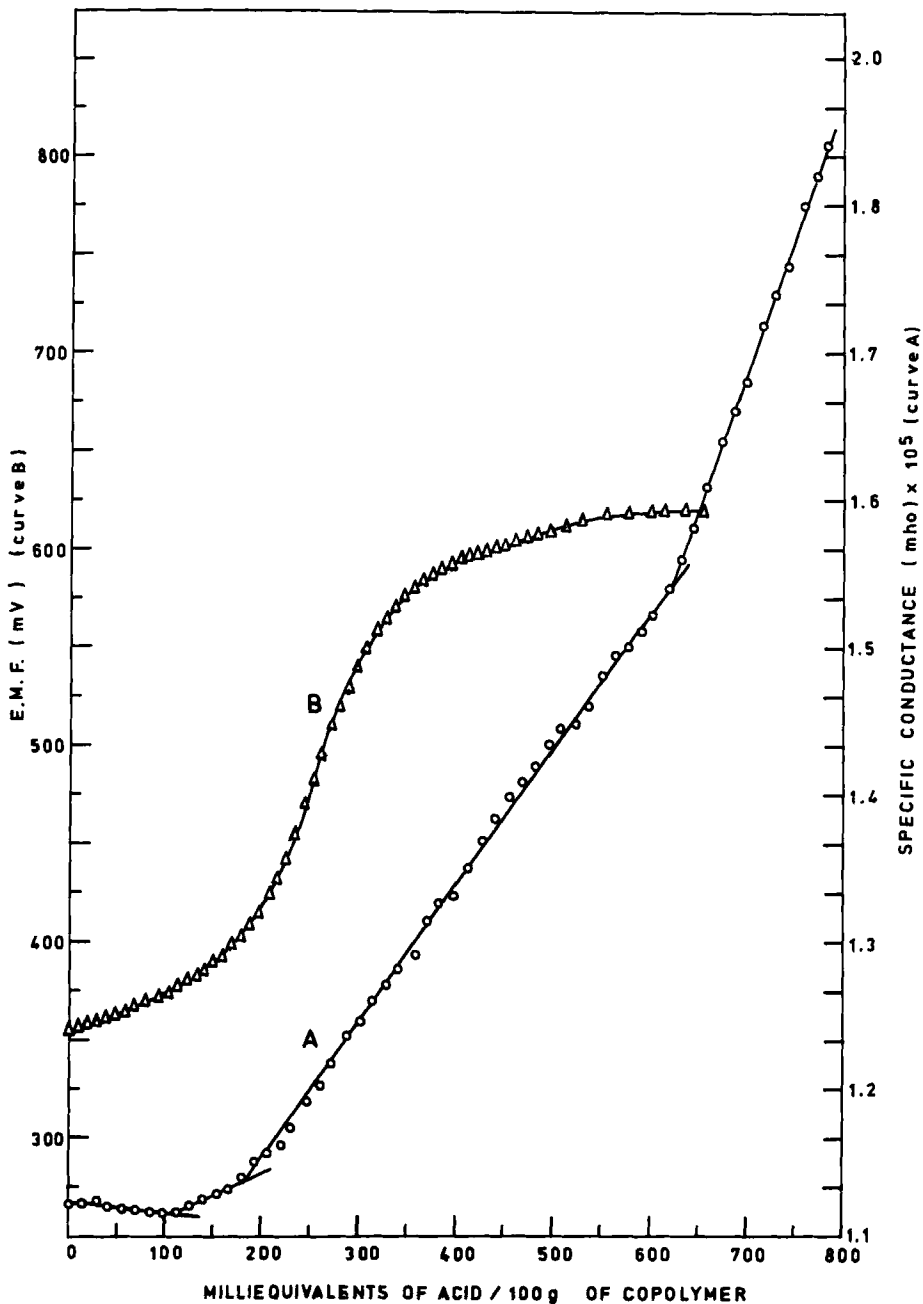


FIG. 10. Titration curves of fraction 3 in glacial acetic acid with perchloric acid as titrant: (A) conductometric curve; (B) potentiometric curve.

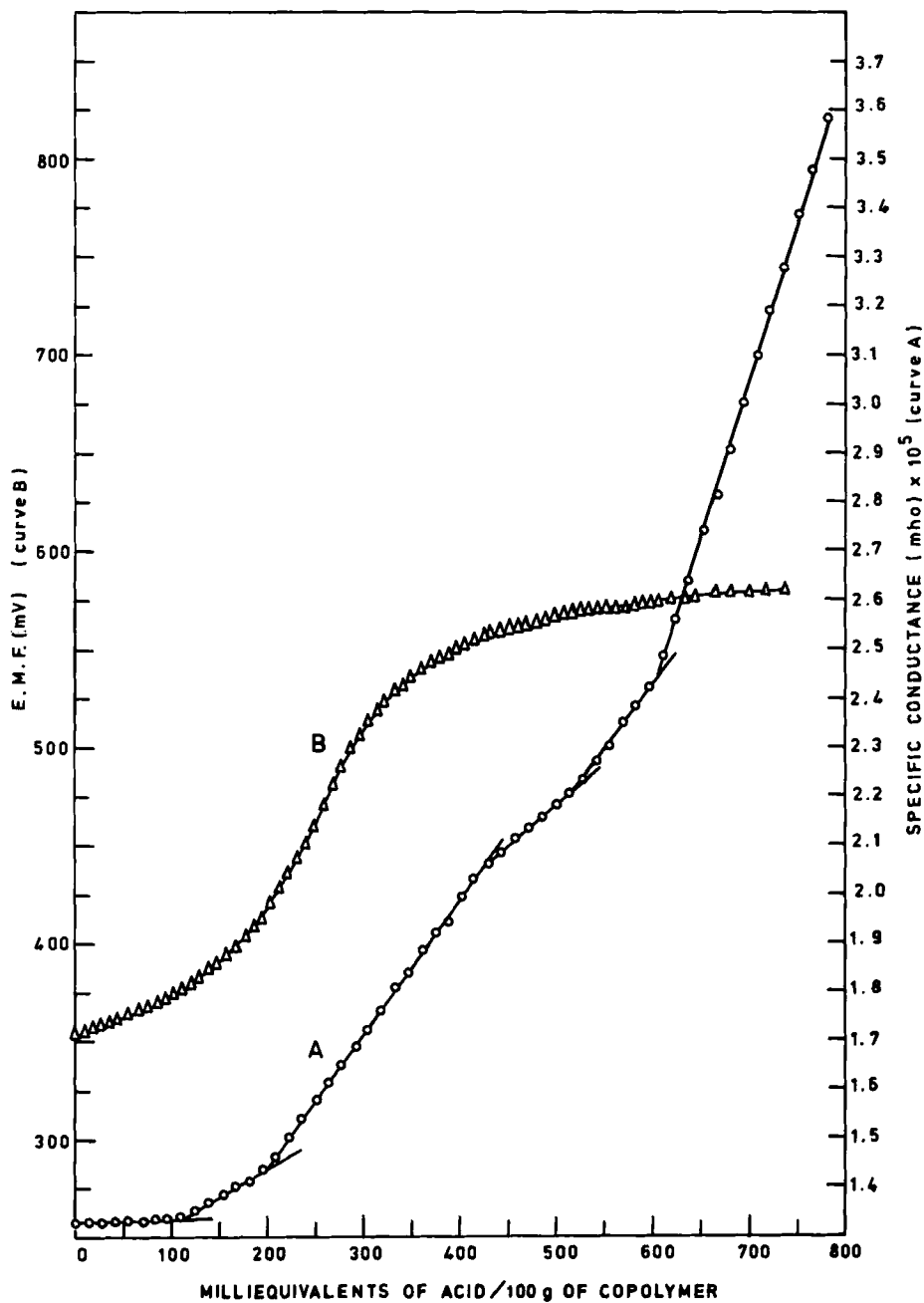


FIG. 11. Titration curves of fraction 4 in glacial acetic acid with perchloric acid as titrant: (A) conductometric curve; (B) potentiometric curve.

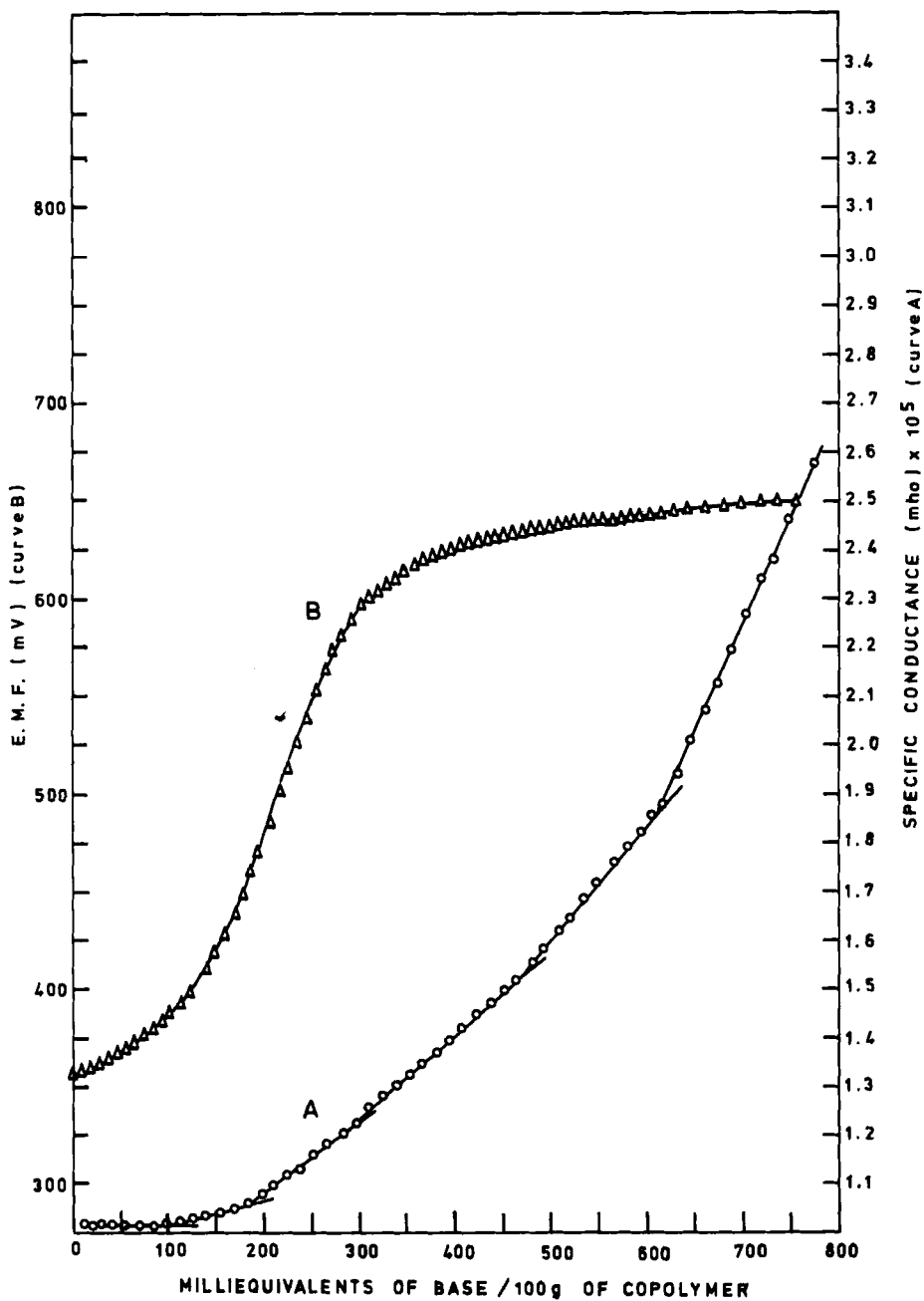


FIG. 12. Titration curves of fraction 5 in glacial acetic acid with perchloric acid as titrant: (A) conductometric curve; (B) potentiometric curve.

TABLE 1. Observed Amounts of Acidic and Basic Groups in p-Aminobenzoic Acid (PAB)/Formaldehyde/p-Bromoaniline (PBA) Copolymer and its Fractions

Copolymer	Br content (%)	Average DP	Smallest interval	PAB:PBA molar ratio	Total NH ₂ groups (meq/100 g of copolymer)		Total COOH groups (meq/100 g of copolymer)	
					Calcd ^a	Found	Calcd ^a	Found
Conglomerate	30.56	17.4	35	0.73:1.27	610	600	222	220
Fraction I	39.96	27.7	20	0.19:1.81	554	555	52	60
Fraction II	45.72	20.3	27	0.10:1.90	549	580	27	30
Fraction III	12.75	18.0	35	1.47:0.53	632	625	468	480
Fraction IV	17.12	15.2	40	1.29:0.71	610	605	424	415
Fraction V	24.77	10.0	69	0.97:1.03	600	610	290	295

^aOn the basis of Br estimation.

number of inflections observed in the corresponding potentiometric curves was comparatively smaller. The discrepancy in the nature of the conductometric and potentiometric curves is expected, because factors such as ion association, intramolecular hydrogen bonding, and different degrees of dissociation between various acid-anion or base-cation complexes in a medium of low dielectric constant will influence the conductometric curve much more than the potentiometric curve. Kolthoff and co-workers [4-6] also observed such behavior in the conductometric titration of weak acids in nonaqueous solvents.

The fact that some of the NH_2 or COOH groups of the copolymer molecule are neutralized earlier than others indicates that they have a stronger basic/acidic character. Sprengling [7] attributed the hyperacidity of *o,o'*-dihydroxydiphenylmethane compounds to intramolecular hydrogen bonding. Another possible reason for the difference in the acidic/basic strengths of the groups, is the presence of different sequence combinations of repeating units in the copolymer chain. It may also be possible that the number of functional groups involved in the formation of intramolecular hydrogen bonds may influence the acidic/basic strengths of the groups. Infrared [8] and conformational [9] studies also revealed the presence of hydrogen bonding in such compounds. The infrared spectra of all the fractions and the conglomerate showed fairly sharp absorptions in the range $3450\text{-}3600\text{ cm}^{-1}$ and $3070\text{-}3350\text{ cm}^{-1}$, showing the probable presence of $\text{H}\cdots\text{O}\cdots\text{H}$ and $\text{N}\cdots\text{H}\cdots\text{N}$ intramolecular hydrogen bonding.

An important aspect of the study is that nonaqueous titrations may provide a fairly elegant method of estimation of relative amounts of various repeating units present in a copolymer chain.

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