Titration Curves of Some Mixtures of Structurally and Molecularly Uniform p-Cresol Formaldehyde Condensates in Nonaqueous Media

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ABSTRACT

Some o,o'-dihydroxydiphenylmethane type of synthetic compounds of uniform constitution and molecular weight have been prepared by stepwise synthesis. These synthetic novolaks, when mixed in various molecular proportions, resemble p-cresol formaldehyde condensation polymers. A study has been made on the titration curves of the mixtures of synthetic compounds in nonaqueous media. A large number of breaks and inflections have been observed in the titration curves, and they occur in simple multiples of the calculated amount of base required to neutralize OH groups in the various novolak molecules independently. These observations have been interpreted in terms of ion association, dielectric constant of the solvent, and intramolecular hydrogen bond formation between neighboring OH groups of the novolak molecules.

Some preliminary titrimatric studies in nonaqueous medium on linear condensation polymers of phenolic compounds with formaldehyde revealed that the degree of polymerization (DP) of such products could be evaluated conveniently [1]. Some of these products, which are important intermediates in the Bakelite Industry, have a o,o'-dihydroxydiphenylmethane type of structure. These condensation polymers are heterogeneous systems and are made up of molecules of different chain lengths. It was considered of interest to prepare, according to known methods, some o,o'-dihydroxydiphenylmethane type of synthetic compounds of uniform constitution and molecular weight. These synthetic novolaks when mixed in various molecular proportions should resemble p-cresol-formaldehyde condensation polymers. Keeping this fact in view and with the available information on the titration curves of the pure synthetic compounds [2], a study has been made on the titration curves of mixtures of synthetic compounds of uniform structure and molecular weight. The titration curves indicated some very interesting and unexpected features. A large number of breaks have been observed in the conductometric titration curves, and they occur in simple multiples of the calculated amount of base required to neutralize the OH groups in the various novolak molecules independently. One would normally expect these OH groups to have more or less the same acidic strength, in which case the neutralization of many of them would merge and take place in a single step. An attempt has been made in this paper to correlate these observations with factors such as ion association, dielectric constant of solvent, and intramolecular hydrogen bond formation between neighboring OH groups of the novolak molecules.

EXPERIMENTAL

For the preparation of the following structurally and molecularly uniform p-cresol formaldehyde condensates (I, II, and III), the methods of Kammerer and coworkers were followed [3, 4]. The hexanuclear compound I (Br-6-Br) was prepared by condensing 0.01 moles of 2,2'-dihydroxy-5,5' dimethyldiphenylmethane (H-2-H) with slightly more than 0.02 mole of 3-bromo-3'-hydroxymethyl-2,2'-dihydroxy-5,5'-dimethyldiphenylmethane (Br-2-CH_2OH) in the presence of concentrated HCl as catalyst. The reaction mixture was heated at 130° for 1 hr, the fused mass was dissolved in dioxane, and finally it was precipitated with methanol. The helptanuclear compound II (Br-7-Br) was synthesized by condensing 0.01 mole of 2,6-bis-(2-hydroxy-5-methylbenzyl-4-methylphenyl) [5] (H-3-H) with a little more than 0.02 mole of 3-bromo-3-hydroxymethyl-2,2'-dihydroxy-5,5'-dimethldiphenylmethane (Br-2-CH_2OH) in the presence of HCl as catalyst. The reaction product was worked out as described for Compound I. The dibromo-octanuclear compound III

I   N = 4

II   N = 5

III   N = 6
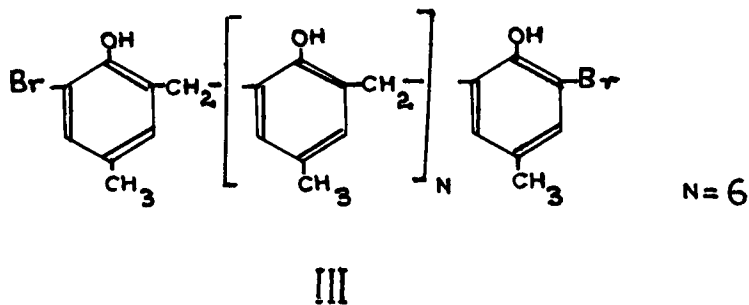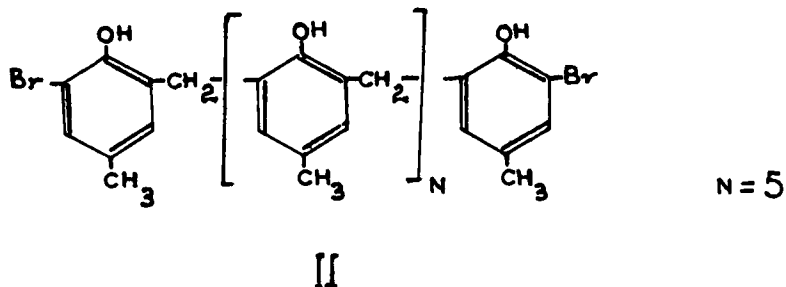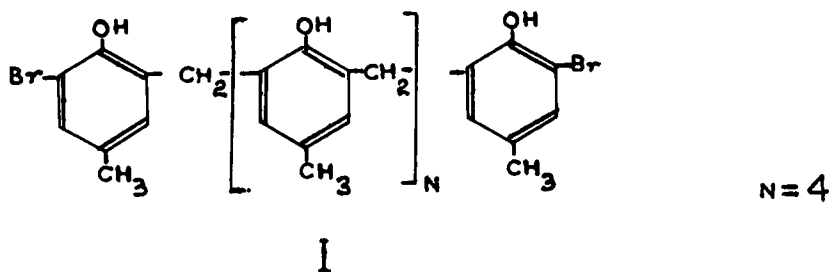
(Br-8-Br) was prepared by condensing 0.01 mole of 2,2'-dihydroxy-3,3'-di-(2-hydroxybenzyl)-diphenylmethane (H-4-H) with slightly more than 0.02 mole of 3-bromo-3'-hydroxymethyl-2,2'-dihydroxy-5,5'-dimethyldiphenylmethane (Br-2-CH$_2$OH) in the presence of concentrated HCl as catalyst and the reaction product worked out as described earlier.

    A Radiometer pH-meter (Model pHM 26C) with glass electrode (G 202B) and a calomel electrode (K 401) as reference was used for

pH titrations. A Leeds and Northrup 4959 Electrolytic Conductance
Bridge was used for conductometric titrations. The titration vessel
was stirred with a magnetic stirrer which was switched off during
each measurement. The titrations were performed at room tempera-
ture and 2 to 3 min was given after each addition of titrant to obtain
equilibrium readings. Approximately 0.05 g of the mixture of the
various compounds was used for each titration in a volume of 35 ml
solvent. The titrant base was standardized daily. Acetone was used
as the medium and sodium methoxide as the titrant base for both the
conductometric and potentiometric titrations. After a series of
preliminary investigations, the above solvent and titrant were found
to be most suitable for the resolution of the polybasic compounds [2].
The reproductibility of each titration curve has been checked and found
to be within ±2 to 3%.

RESULTS AND DISCUSSION

In Figs. 1-3 the conductometric and potentiometric titration curves
of the synthetic compounds III and II in the molar ratios of 1:1, 2:1, and
1:2 (Br-8-Br:Br-7-Br), respectively, in acetone with sodium methoxide
as titrant base are presented. The conductometric titration curve
(Curve A of Figs. 1-3) for each of the above mixtures showed a number
of sharp breaks. These breaks occur in multiples of a certain amount
of added base. Of course, this amount of base is different for each of
the mixtures. From the values obtained at the various breaks in the
titration curves, it seems that most of the OH groups out of the 15
OH, say in the 1:1 mixture, appear to react independently of one
another with the base. The amount of base, expressed in meq/100 g
of the mixture, which would be required if all OH groups in the various
mixtures were neutralized, one after the other, could be calculated as
follows.

Let the mixture contains "X" g of Compound II and "Y" g of
Compound III. Then Compound II contributes $X/986 \times 7000$ meq of OH
groups to the mixture; the contribution of Compound III is $Y/1106 \times
8000$ meq of OH groups (986 and 1106 are the molecular weights of the
Compounds II and III, respectively). Hence the total number of OH
groups per 100 of the mixture is

$$\frac{\left[\dfrac{X}{986} \times 7000 + \dfrac{Y}{1106} \times 8000\right]}{X + Y} \times 100$$

Thus if all the OH groups are neutralized in 15 equal steps, each step
would require one-fifteenth of the total base added, e.g., for a 1:1 mix-
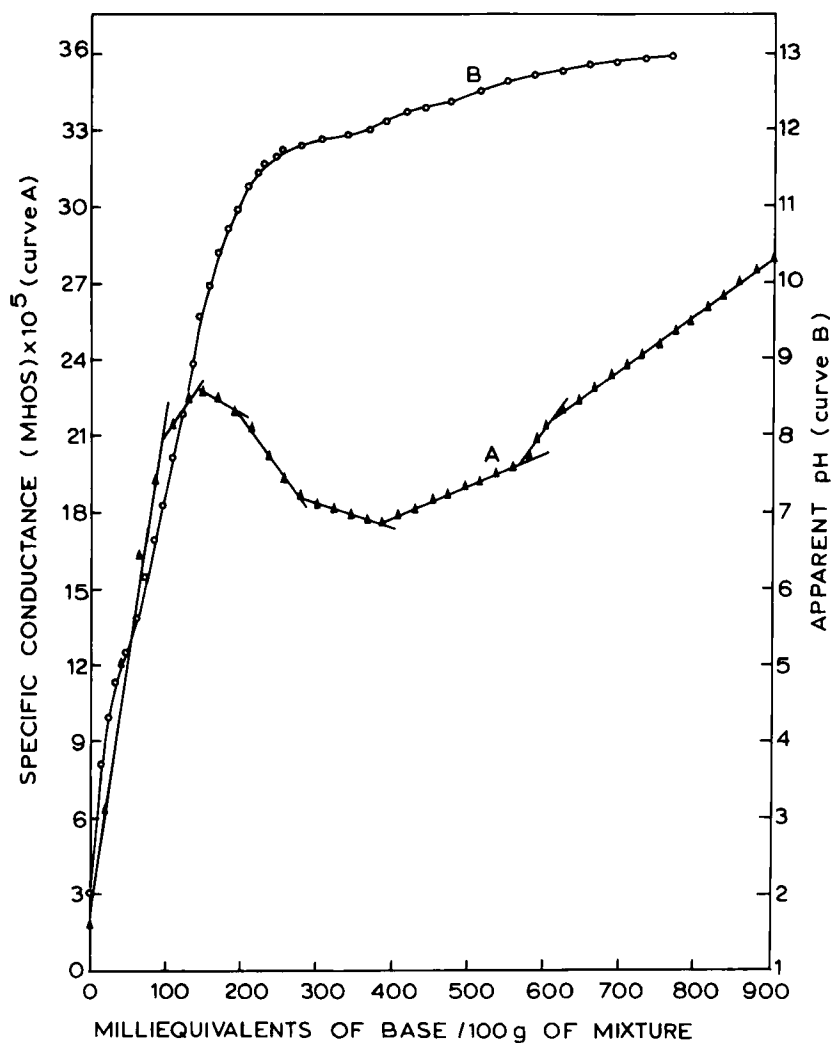ture the value should be 717/15 = 47 meq/100 g of mixture, (Table 1).

FIG. 1. Conductometric (A) and potentiometric (B) curves of
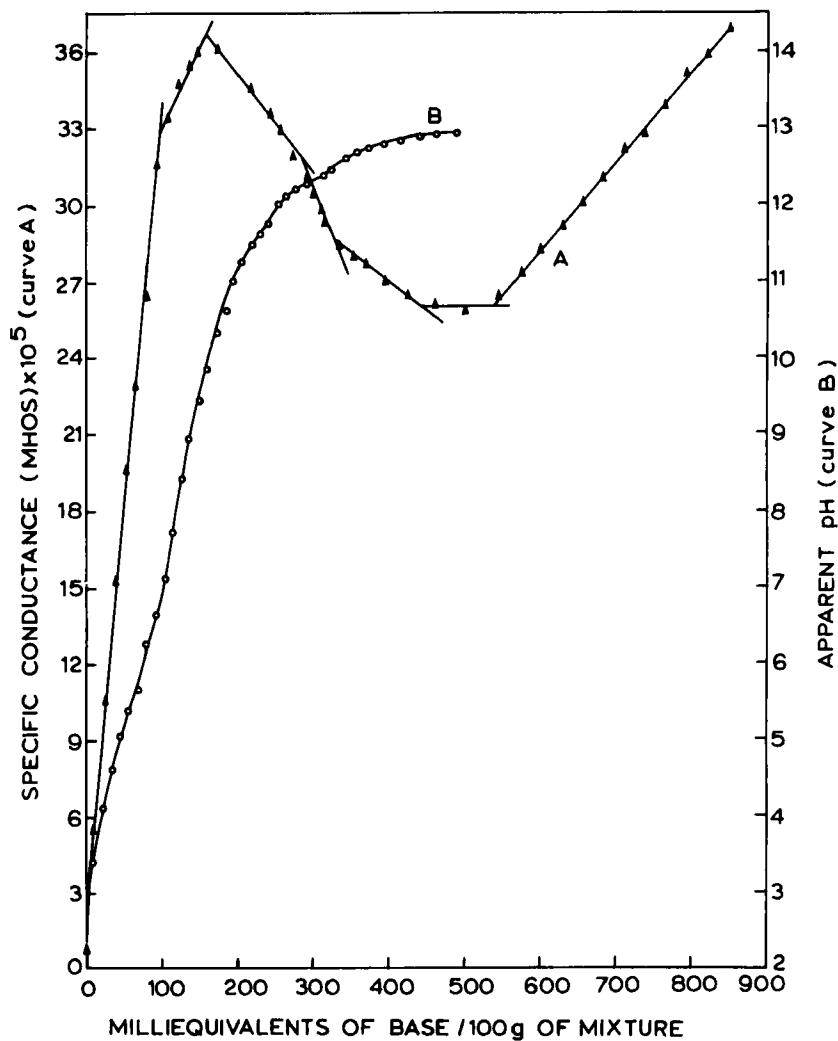1:1 mixture of III and II in acetone with sodium methoxide.

FIG. 2. Conductometric (A) and potentiometric (B) curves of
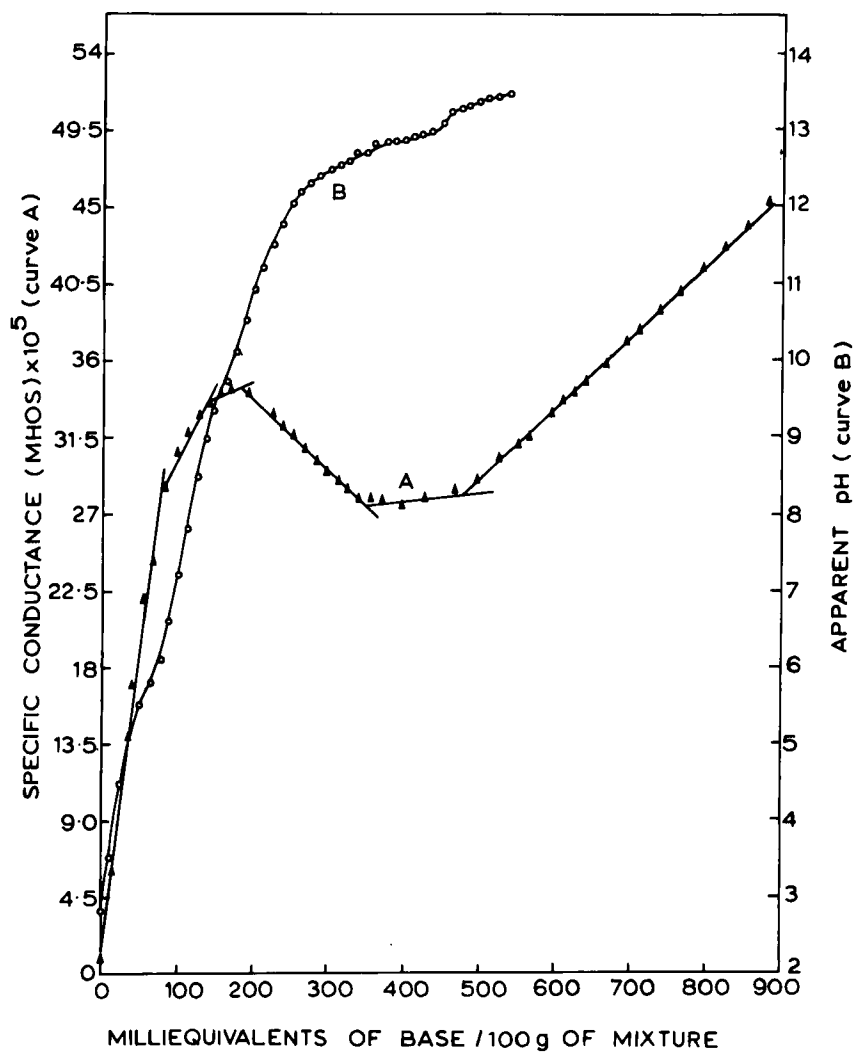2:1 mixture of III and II in acetone with sodium methoxide.

FIG. 3. Conductometric (A) and potentiometric (B) curves of 1:2 mixture of III and II in acetone with sodium methoxide.

TABLE 1. Observed Values (in meq/100 g) of OH Groups

Mixtures	Calculated value for each OH group	1st		2nd		3rd	
		Break	Inflection	Break	Inflection	Break	Inflection
III:II							
1:1	47	95	140	142	375	190	-
2:1	32	95	160	160	320	290	-
1:2	35	75	140	140	180	180	390
III:I							
1:1	50	50	155	105	200	155	250
1:3	26	55	155	130	-	200	-
1:5	18	55	180	140	-	215	-
1:7	14	42	170	100	240	175	-

in the Various Mixtures of Compounds I, II, and III

	4th		5th		6th		7th	
Break	Inflection	Break	Inflection	Break	Inflection	Break	Inflection
280	-	385	-	570	-	610	-
325	-	445	-	545	-	-	-
350	-	480	-	-	-	-	-
250	-	300	-	550	-	-	-
335	-	570	-	-	-	-	-
325	-	390	-	700	-	-	-
355	-	425	-	705	-	-	-

Similarly, the calculated values obtained for the 2:1 and 1:2 mixtures of III and II are 32 and 35 meq/100 g of mixture, respectively. Surprisingly enough, the breaks in the conductometric titration curves (Curve A in Figs. 1-3) occur in simple multiples of 47, 32, and 35 meq of base/100 g of mixture for 1:1, 2:1, and 1:2 compositions, respectively. This clearly indicates that the OH groups in the various mixtures react with the base independently of one another. However, some of the OH groups merge because of their almost identical intrinsic dissociation constants and are neutralized in a single step. This probably explains the occurrence of distinct breaks in the conductometric titration curves in multiples of definite intervals. The corresponding potentiometric curve (Curve B of Figs. 1-3) of each of the three mixtures also showed a very sharp inflection followed by one or two weak inflections. These inflections also occur in multiples of 47, 32, and 35 meq of base/100 g of mixture for 1:1, 2:1 and 1:2 compositions, respectively. Of course, the coincidence of the potentiometric and conductometric curves for a given composition does not refer to the presence of an inflection for every break in the conductometric curve. This coincidence only refers to the simple multiples of the above-calculated amount of base.

It was considered of interest to see whether the OH groups in the two different novolok molecules will continue to react with the base independently of one another when the molar proportion of one of the components in a mixture is slowly increased from 1:1 to 1:7. The potentiometric and conductometric titration curves of synthetic compounds III and I in the molar proportion of 1:1, 1:3, 1:5, and 1:7, respectively, are presented in Figs. 4-7. Assuming independent neutralization of OH groups in the various mixtures, the calculated values of base are 50, 26, 18 and 14 meq/100 g of mixtures, respectively. As expected, the conductometric titration curves of 1:1, 1:3, 1:5, and 1:7 mixtures (Curve A of Figs. 4-7) show distinct breaks which occur in multiples of 50, 26, 18, and 14 meq of base/100 g of mixture, respectively. The corresponding potentiometric curves (Curve B of Figs. 4-7) of each of the mixtures showed a very sharp break followed by a weak inflection. These inflections also occur in simple multiples of the above calculated amounts of base for the respective mixtures.

A noteworthy feature of all the conductometric titration curves is the initial sharp rise in conductance followed by a steep fall and then a subsequent increase in conductance. It has been invariably observed that a steep fall in conductance almost coincides with the sharp inflection of the potentiometric curve for the respective mixture. This hyperacid character in novolak molecules has been explained in terms of intramolecular hydrogen bond formation between neighboring OH groups [6, 7]. The presence of intramolecular hydrogen bonding in such compounds has also been shown in IR and conformational studies [8, 9]. The IR spectra of all compounds studied indicated sharp
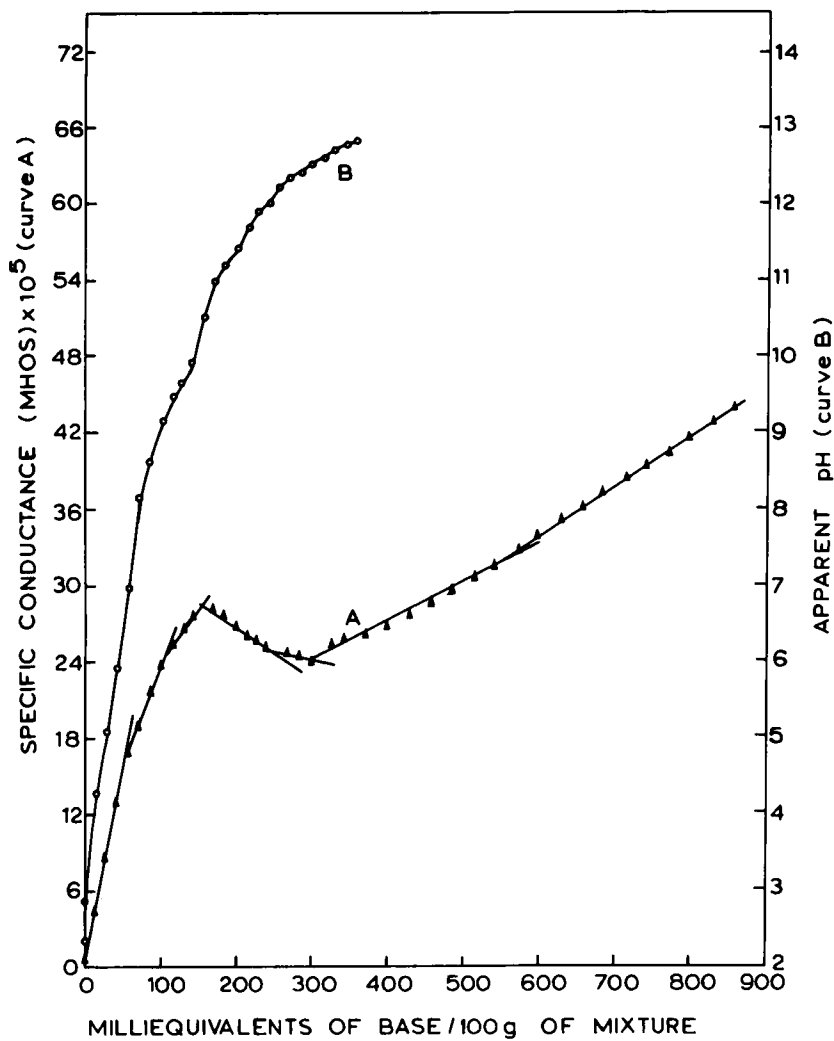
FIG. 4. Conductometric (A) and potentiometric (B) curves of 1:1 mixture of III and I in acetone with sodium methoxide.
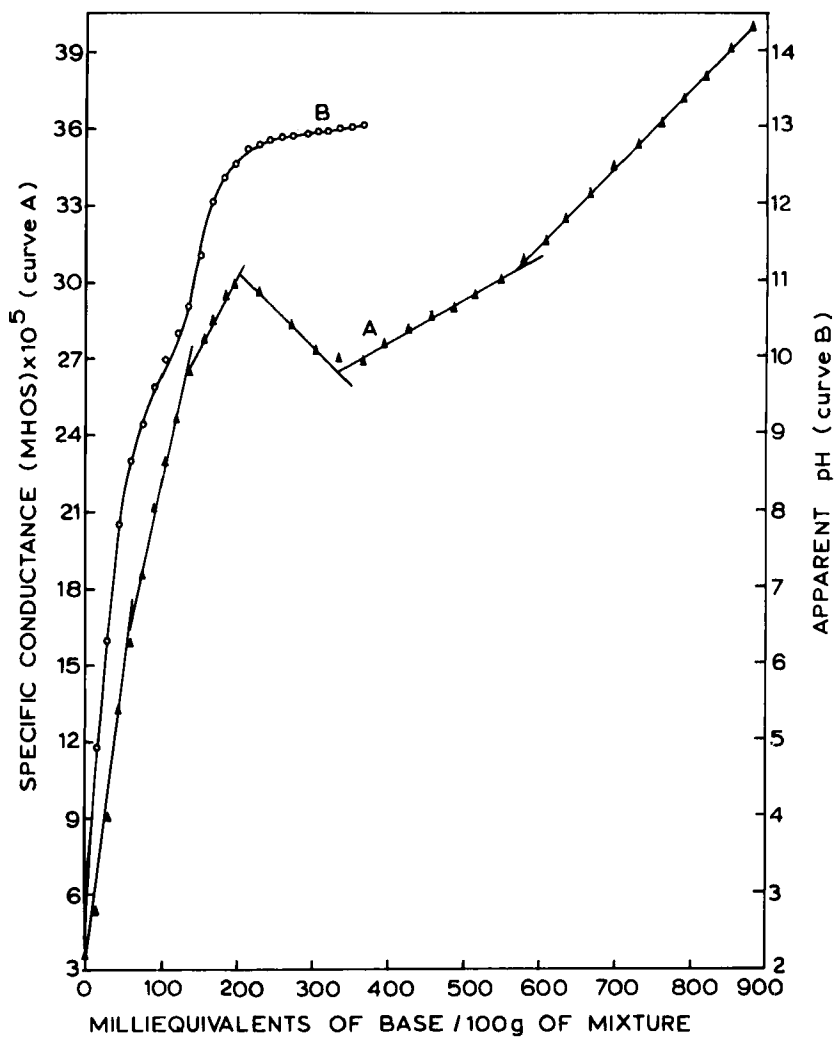
FIG. 5. Conductometric (A) and potentiometric (B) curves of 1:3 mixture of III and I in acetone with sodium methoxide.
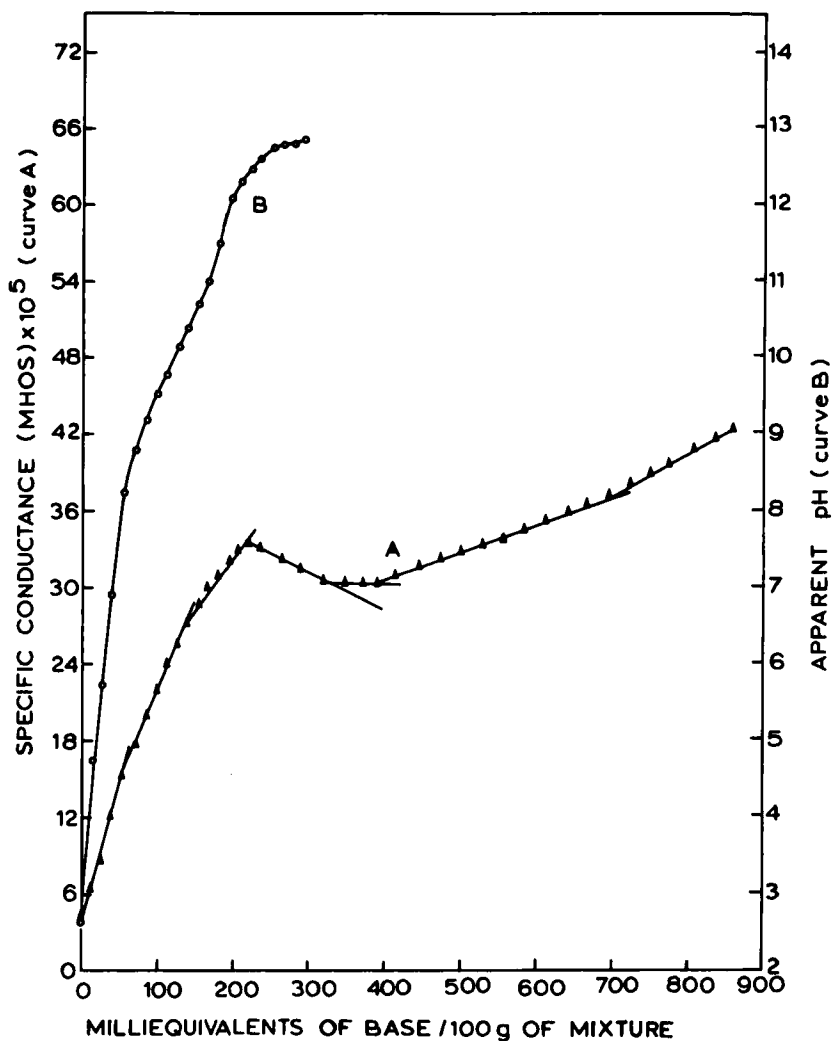
FIG. 6. Conductometric (A) and potentiometric (B) curves of 1:5 mixture of III and I in acetone with sodium methoxide.
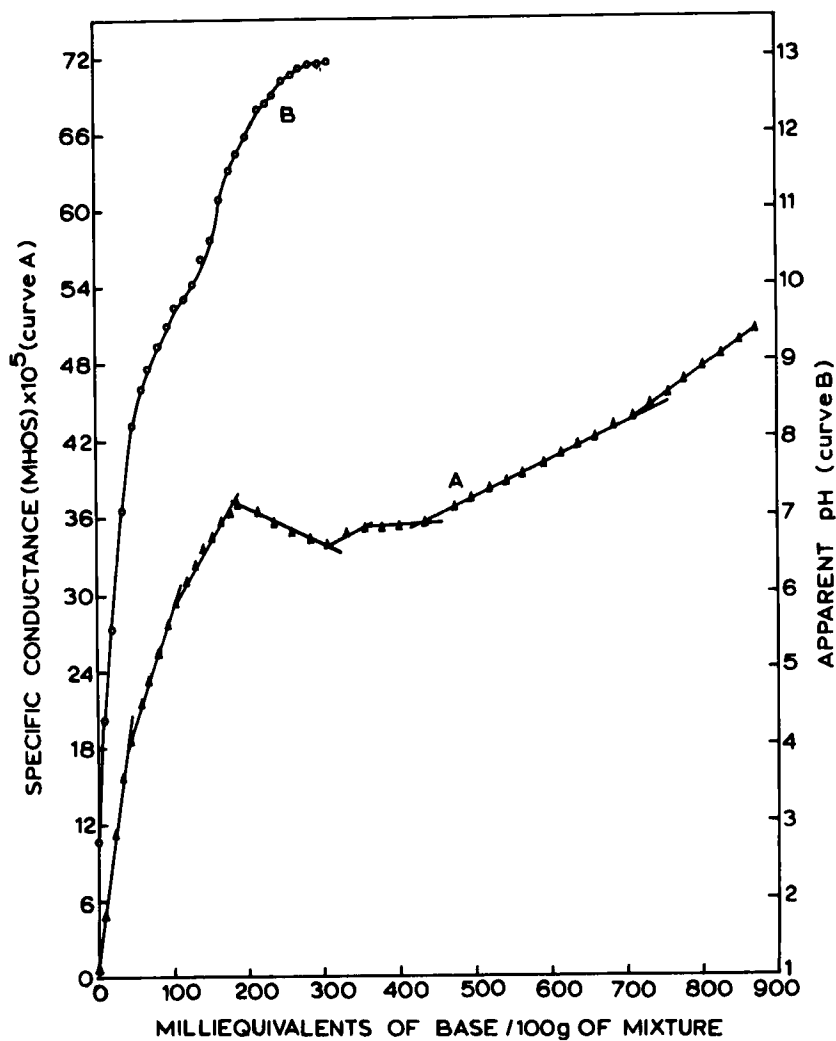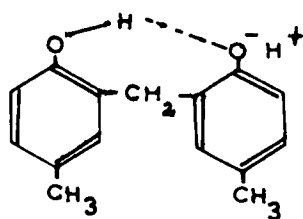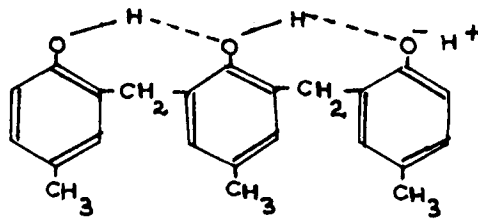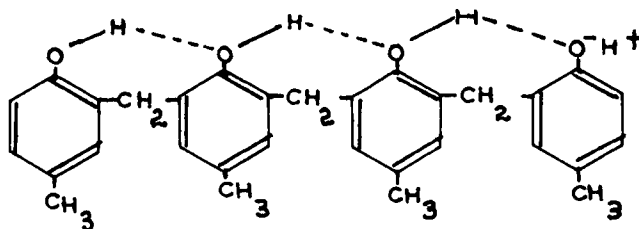
FIG. 7. Conductometric (A) and potentiometric (B) curves of 1:7 mixture of III and I in acetone with sodium methoxide.

IV

V

VI

absorptions in the range 3450 to 3600 cm^{-1}, showing the probable
presence of intramolecular hydrogen bonding. Therefore, it is expected
that the first sharp inflection in the potentiometric curve of each of the
mixtures shows the neutralization of all the hyperacid hydroxyls of
both the novolak molecules. The sharp fall in conductance may be in-
terpreted as due to two factors: 1) an increased negative change on the
anion and 2) the low dielectric constant of the medium. Both these
factors strongly favor ion association, and consequently a fall in con-
ductance is expected. Another important difference between the
conductometric and potentiometric titration curves is the presence of
a large number of distinct breaks in the former compared to a very
few inflections in the corresponding potentiometric curve. One can
expect such a discripency in view of the fact that such factors, as ion
association, dielectric constant of the medium, and acid-anion complex
formation will influence the conductometric curve much more than to
potentiometric curve. Moreover, the difference in the degree of dis-
sociation of the various acid-anion complexes, which may have been
formed in a medium of low dielectric constant, may be responsible for
the neutralization of OH groups in distinct steps. Such a homoconjuga-
tion has also been observed by Kolthoff and co-workers [10-12].

One can thus conclude that nonaqueous titration may provide a very versatile method for studying the dissociation behavior of functional groups in polymer molecules.

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