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## Effect of Hydrogen Bonding on the Dissociation of Some Mixtures of Phenolic Oligomers in Nonaqueous Media

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### ABSTRACT

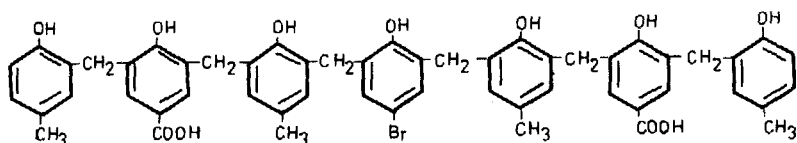
Some structurally and molecularly uniform phenolic oligomers with additional functional groups have been prepared by known methods of stepwise synthesis, and their dissociation behavior in nonaqueous solvent has been studied by electrometric titration techniques. Hyperacidity and stepwise neutralization of some of the functional groups in the oligomer molecules have been interpreted in terms of intramolecular hydrogen bonding, homoconjugation, and ion association in a medium of low dielectric constant.

In recent years nonaqueous solvents have been widely used as media in electroanalytical studies. However, these techniques have not been used so much in the field of synthetic polymer chemistry. Some preliminary investigations on phenolic polymers revealed that electrometric titration techniques in nonaqueous solvents may provide a reasonably simple and elegant method of studying the dissociation behavior of phenolic polymers having acidic/basic functional groups [1-3]. Some of these phenolic polymers and oligomers are

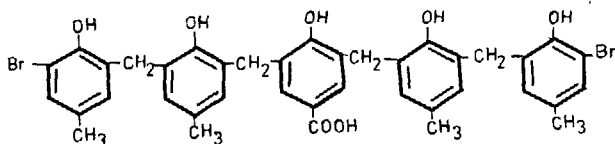
characterized by the presence of intramolecular hydrogen bonding [4-6]. Since structures of many of the phenolic oligomers with additional functional groups are known from their stepwise synthesis [7], structural features of the oligomers could be directly correlated with their titration curves in nonaqueous media. A study has been made of the titration curves of the various mixtures of the oligomers, because such mixtures resemble phenol-formaldehyde condensation polymers. The titration curves of these mixtures showed some characteristic features which could be correlated with intramolecular hydrogen bonding, homoconjugation, and ion association in a medium of low dielectric constant.

### EXPERIMENTAL

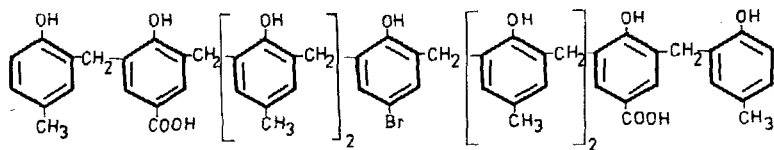
The preparation of the oligomeric compounds I-III was by the methods of Kammerer and Haub [7].



I



II



III

The details of the preparative methods have been described elsewhere [2].

A Leeds and Northrup 4959 electrolytic conductance bridge was used for conductometric titrations and a Radiometer pH meter (Model PHM 260) with glass electrode (G 202 B) and a calomel electrode

(K 401) as reference was used for pH titrations. The titration vessel was stirred with a magnetic stirrer which was switched off during each measurement. The titrations were performed at room temperature, and 2-3 min was given after each addition of titrant to obtain equilibrium readings. Approximately, 0.05 g of compound 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 and tetramethylammonium hydroxide (TMAH) as titrants. The above solvent and titrants were found to be most suitable for resolution of polybasic acids [8]. The reproducibility of each titration curve has been checked and found to be within  $\pm 2-3\%$ .

## RESULTS AND DISCUSSION

In Figs. 1-4, the conductometric and potentiometric titration curves of the oligomers I and II in II:I molar ratios of 1:1, 1:2, 1:4, and 1:8, respectively, in acetone with sodium methoxide and TMAH as titrant bases are presented. The conductometric titrations have been performed only with both the titrants, because, potentiometric titration curves did not give any additional information with TMAH as titrant base.

The conductometric curve with sodium methoxide as titrant (e. g., curves A of Figs. 1-4) 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. The conductometric curves of the same mixtures with TMAH as titrant base (e. g., curves B of the Figs. 1-4), also indicated several distinct breaks. For a particular mixture, irrespective of whether it is titrated with sodium methoxide or TMAH as titrants, the breaks occur in multiples of the same amount of added base. From the values obtained at the various breaks in the titration curves, it seems that most of the acidic functional groups out of 15 (e. g.,  $2 + 1 = 3$  COOH and  $7 + 5 = 12$  phenolic OH groups), say in the 1:1 mixture of oligomers I and II, appear to react independently of one another with the base. The amount of base, expressed in milliequivalents per 100 g of the mixture, which would be required if all the acidic groups in the various mixtures were neutralized, one after the other, could be calculated as follows.

Let the mixture X grams of the oligomer (I) and Y grams of the oligomer (II). Then the oligomer (I) contributes  $(X/953)$  9000 meq of acidic functional groups to the mixture; the contribution of oligomer (II) is  $(Y/776)$  6000 meq of acidic functional groups (953 and 776 are the molecular weights of the oligomers I and II respectively). Hence, the total amount of acidic groups (e. g., COOH and OH), per 100 g of the mixture is

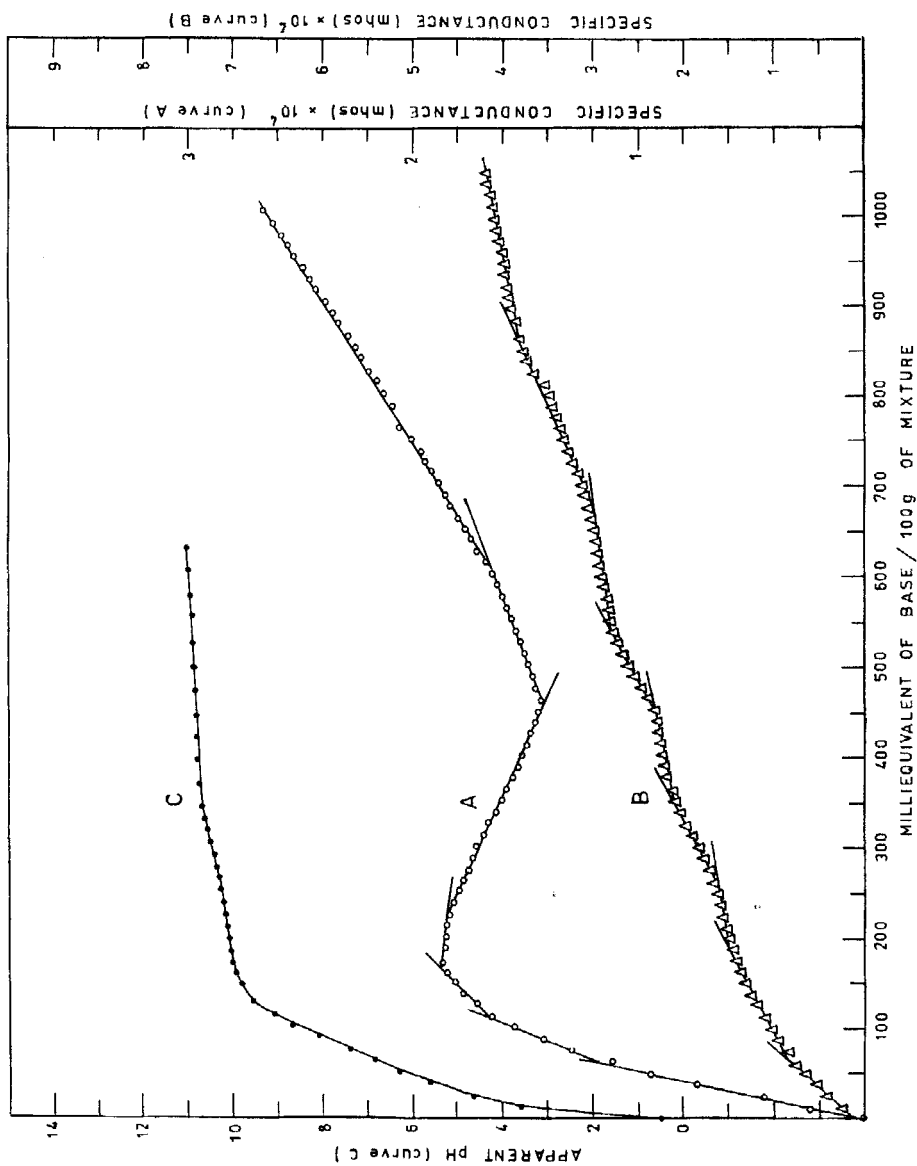


FIG. 1. Conductometric and potentiometric curves of 1:1 mixture of II and I: (A) conductometric NaOCH<sub>3</sub> titrant; (B) conductometric, TMAH titrant; (C) potentiometric.

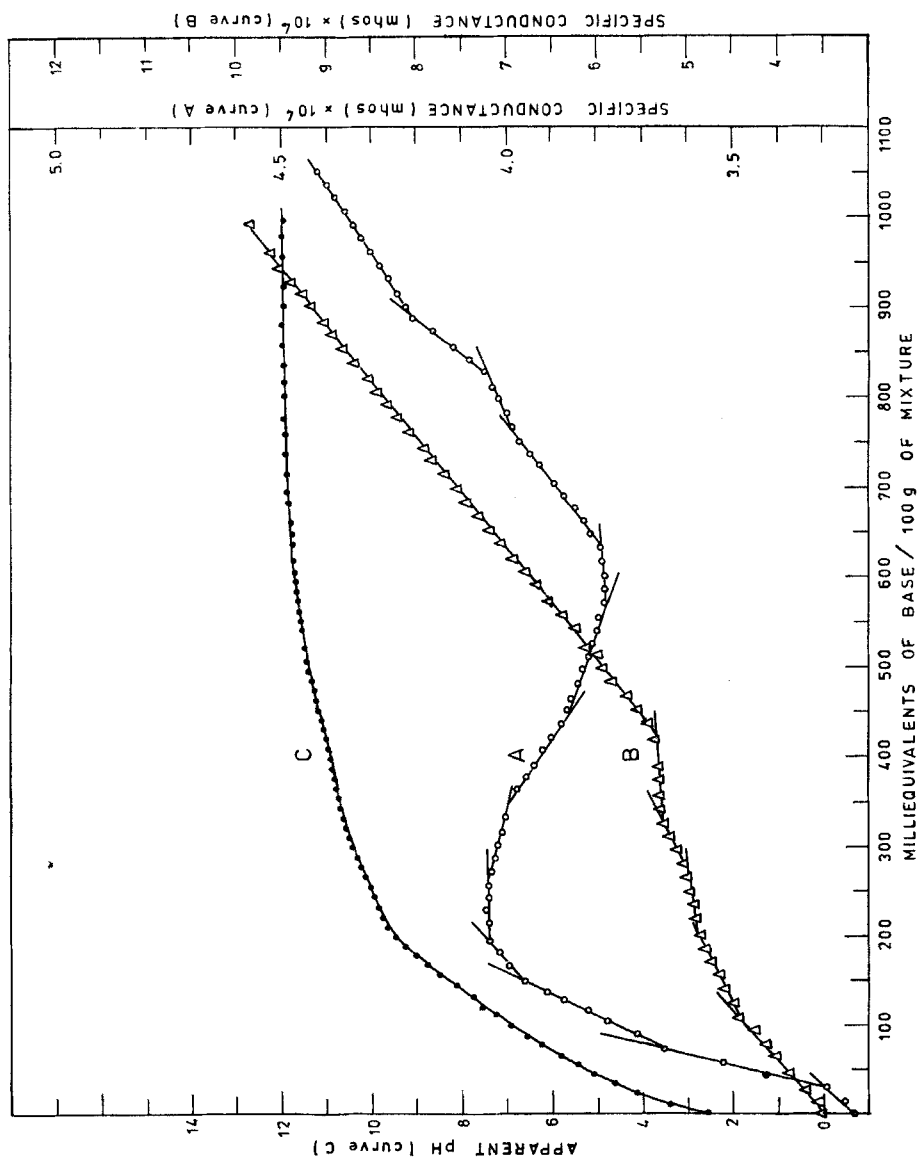


FIG. 2. Conductometric and potentiometric curves of 1:2 mixture of II and I: (A, B, C) as in Fig. 1.

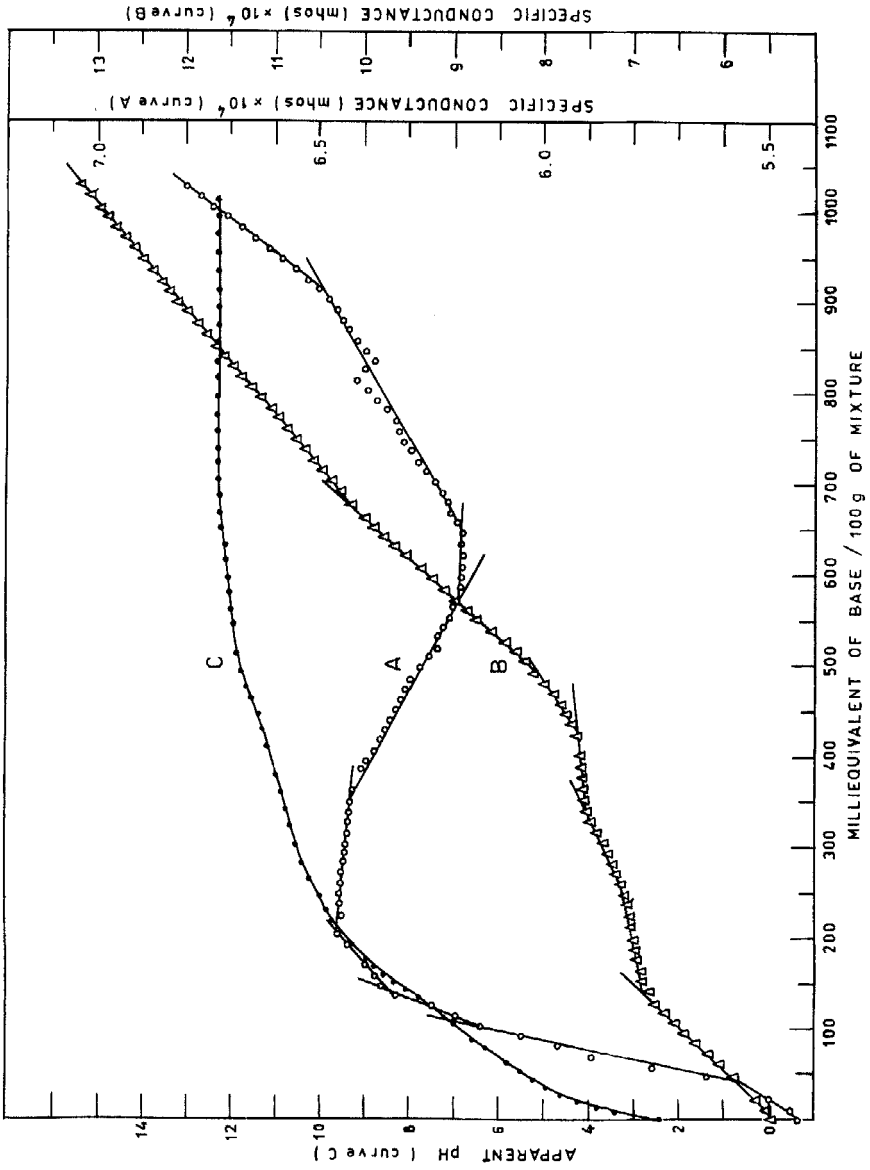


FIG. 3. Conductometric and potentiometric curves of 1:4 mixture of II and I: (A, B, C) as in Fig. 1.

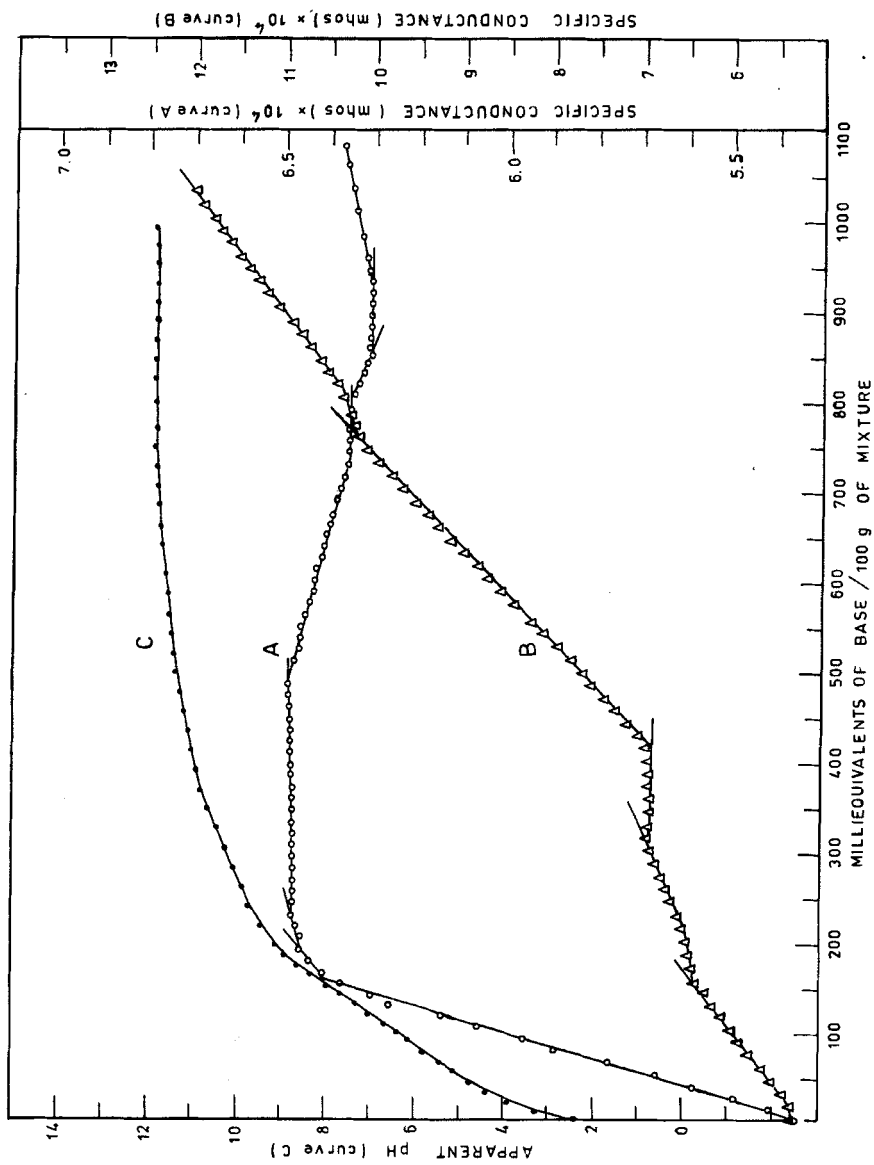


FIG. 4. Conductometric and potentiometric curves of 1:8 mixture of II and I: (A, B, C) as in Fig. 1.



$$T = \frac{(X/953) 9000 + (Y/776) 6000}{X + Y} \times 100$$

Thus if all the acidic functional groups are neutralized in 15 equal steps, each step should require one fifteenth of the total base; e. g., for the 1:1 mixture, the value should be  $868/15 = 57.85$  meq of base per 100 g of the mixture. Similarly, the calculated values for the 1:2, 1:4, and 1:8 mixtures II and I are 37.3, 21.8, and 11.0 meq base/100 g mixture, respectively. Surprisingly enough, the breaks in the conductometric titration curves (e. g., curves A and B of Figs. 1-4), of each of these mixtures, occur in simple multiples of 57.8, 37.3, 21.8 and 11.0 meq/100 g of mixture, respectively. The corresponding potentiometric curves (e. g., curve C of the Figs. 1 to 4) of each of the above mixtures, showed some weak inflections. However, these inflections also occur in simple multiples of the above calculated values. Of course, the coincidence for the conductometric and potentiometric curves for a given mixture, 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. A fair agreement can be seen (Table 1) between the calculated values and those observed at the successive breaks and inflections of the titration curves.

It is indeed remarkable that the acidic functional groups in the various mixtures react with the base independently of one another. However, some of the functional groups do merge up 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 curves in multiples of a definite interval. The fact that the observed and calculated amounts of acidic functional groups agree, as illustrated in Table 1, leaves no room for doubting this certainly unexpected result. Moreover, when the same mixture is titrated independently by two different titrants, e. g. sodium methoxide and TMAH, the results almost tally within experimental error.

It was considered of interest to see whether the acidic functional groups will continue to react with the base independently of one another when the molecular proportions, and also the nature and size of the oligomer molecules are different. Keeping this in view, potentiometric and conductometric titration of some mixtures of oligomers I and III have been done. Figures 5-8, show the potentiometric and conductometric titration curves of 1:1, 1:3, 1:5, and 1:7 mixtures of the oligomers III and I in acetone with sodium methoxide and TMAH as titrant bases. Assuming independent neutralization of acidic functional groups in the various mixtures, the calculated values for each acidic functional group comes out to be 46.8, 24.7, 16.8, and 12.7 meq base/100 g mixture, respectively. The potentiometric curves of all these mixtures (e. g., curves C of Figs. 5-8),

TABLE 1. Observed Values of the Acidic Groups in the Various Mixtures of Oligomers I and II

Break	II:I = 1:1		II:I = 1:2		II:I = 1:4		II:I = 1:8	
	Curve A	Curve B	Curve A	Curve B	Curve A	Curve B	Curve A	Curve B
1st	60	62	35	110	43	190	155	158
2nd	112	185	75	202	100	260	190	215
3rd	170	280	150	280	145	340	227	307
4th	225	350	195	325	205	430	497	417
5th	462	460	270	430	350	485	740	755
6th	620	550	355	-	575	677	802	815
7th	-	690	450	-	655	-	850	-
8th	-	865	570	-	910	-	930	-
9th	-	-	645	-	-	-	-	-
10th	-	-	770	-	-	-	-	-
11th	-	-	825	-	-	-	-	-
12th	-	-	900	-	-	-	-	-
Calcd amount of base for each functional group <sup>a</sup>	57.85		37.30		21.80		11.00	

<sup>a</sup> Values expressed in milliequivalents of base per 100 g of mixture.

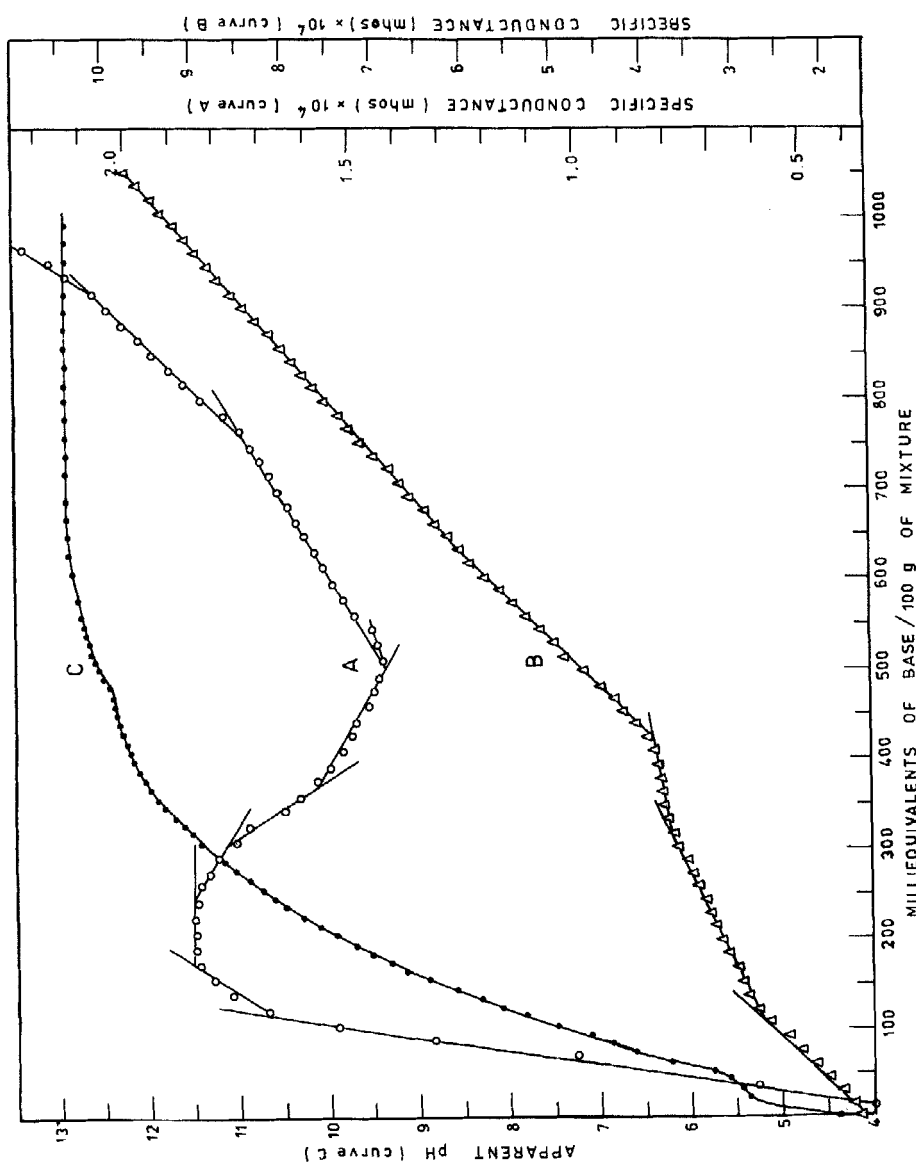


FIG. 5. Conductometric and potentiometric curves of 1:1 mixture of III and I: (A, B, C) as in Fig. 1.

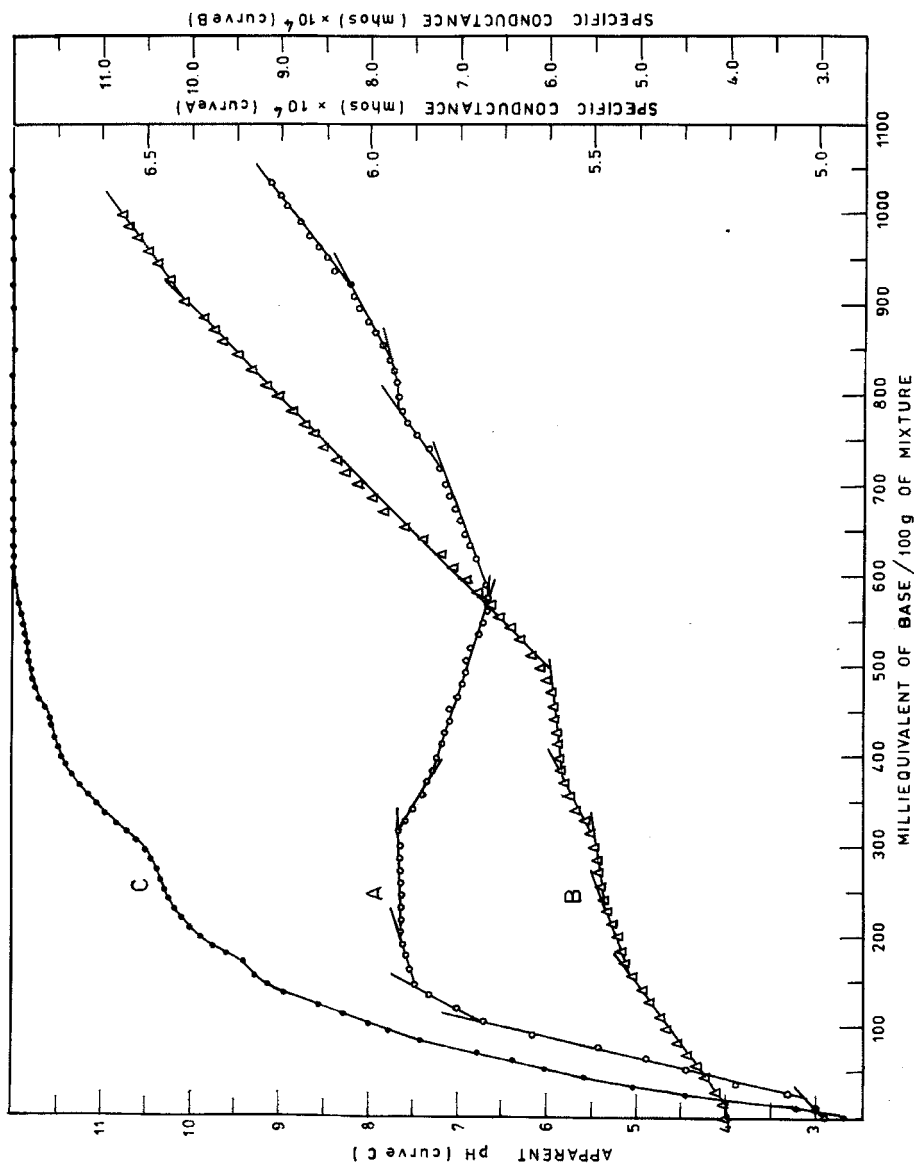


FIG. 6. Conductometric and potentiometric curves of 1:3 mixture of III and I: (A, B, C) as in Fig. 1.

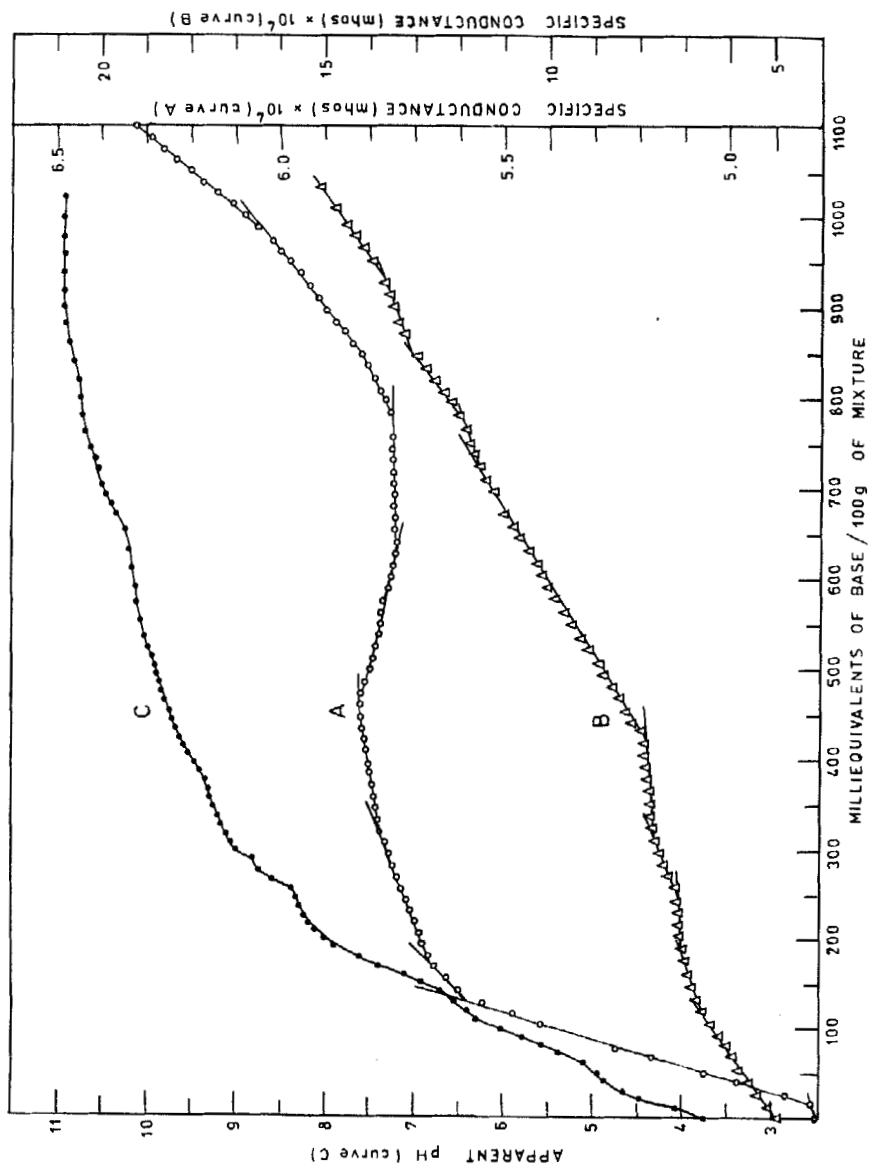


FIG. 7. Conductometric and potentiometric curves of 1:5 mixture of III and I: (A, B, C) as in Fig. 1.

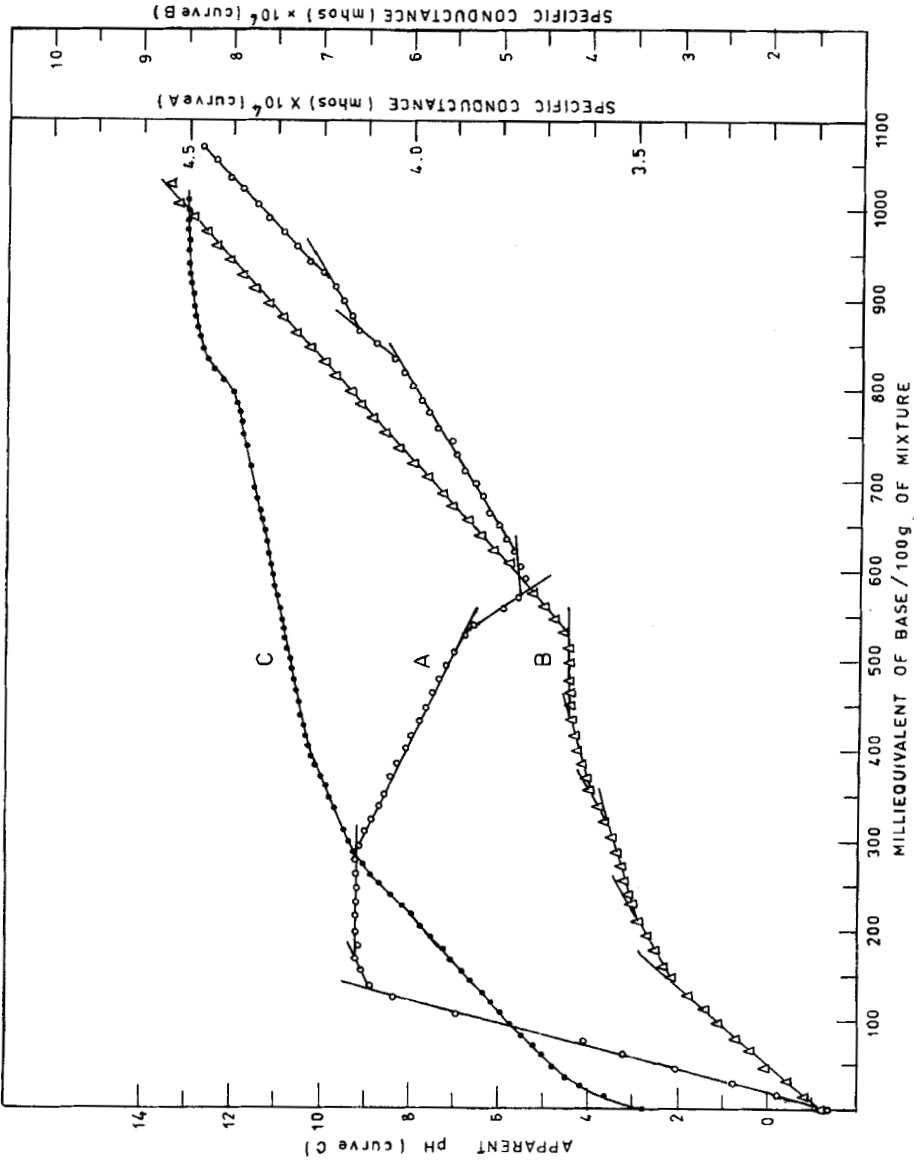


FIG. 8. Conductometric and potentiometric curves of 1:7 mixture of III and I: (A, B, C) as in Fig. 1.

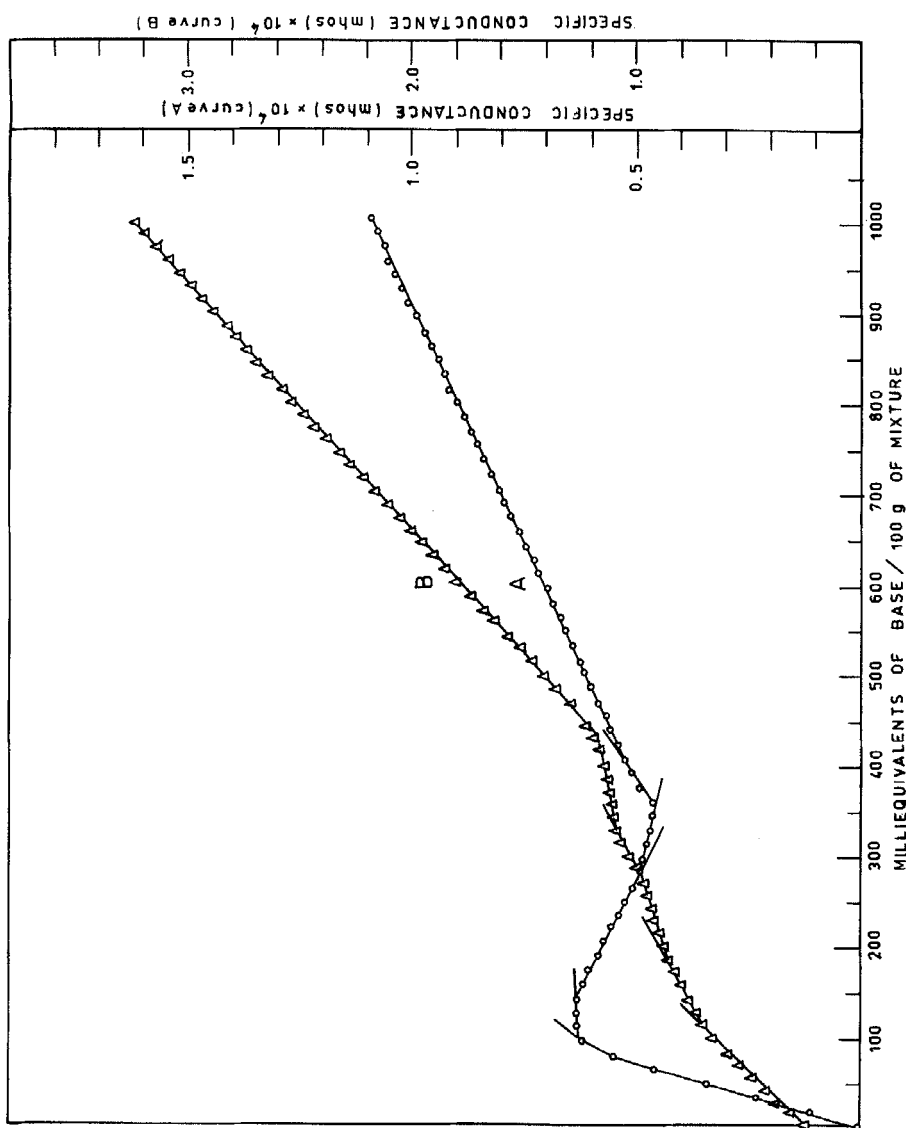


FIG. 9. Conductometric curves of 1:1 mixture of I, II, and III: (A) sodium methoxide titrant, (B) TMAH titrant.

showed two or three inflections each, and they also occur in simple multiples of the calculated values for the respective mixtures.

It was also considered worthwhile to investigate whether these oligomers with additional functional groups, will continue to behave in a similar way, when their number is increased from two to three in the mixture. Figure 9 shows the conductometric titration curves of a 1:1:1 mixture of oligomers I, II, and III, in acetone with sodium methoxide (curve A), and TMAH (curve B) as titrant bases. Since, the potentiometric curves did not give any worthwhile information, therefore, this technique had not been used for this particular mixture. The calculated value of base for each acidic functional group of this mixture is found to be 34 meq/100 g of mixture. As expected from previous experience, the successive breaks in the titration curves occur in simple multiples of the above calculated value. Of course, the final break in both the conductometric curves did not indicate the complete neutralization of the acidic functional groups.

The neutralization of oligomeric compounds in several distinct steps, indicated that some of the OH groups have acquired hyperacid character as a result of intramolecular hydrogen bonding between neighboring groups. The presence of intramolecular hydrogen bonding in such compounds has also been shown from titrimetric [4], infrared [5], and conformational [6] studies. The IR spectra of all the compounds studied by us indicated absorptions in the range  $3450$  to  $3600\text{ cm}^{-1}$ , showing the probable presence of  $\text{O-H} \cdots \text{O}$  intramolecular hydrogen bonding. The initial sharp increase in conductance as well as the inflections in the potentiometric curve, corresponds with the neutralization of hyperacid hydroxyl/carboxyl groups of the compounds. The fall in conductance during subsequent stages in the titration curves with sodium methoxide (curves A of Figs. 1-8), may be interpreted in terms of ion-association. Factors such as increased negative charge on the anion, low dielectric constant of the medium, and small size of cation ( $\text{Na}^+$ ) of titrant base are all likely to favor ion association. Moreover, such a fall in conductance was not seen in the titration curves with TMAH (curves B of Figs. 1-8). This was expected because of the larger size of the titrant cation [ $(\text{CH}_3)_4\text{-N}^+$ ]. Potentiometric curves did not show many distinct steps during the neutralization, because, factors like homoconjugation and difference in the degree of dissociation of various acid-anion complexes which might have been formed in a medium of low dielectric constant may not affect them to that extent. In case of weak acids, such homoconjugation has also been observed by Kolthoff and co-workers [9-11].

In conclusion, one can say that the presence of intramolecular hydrogen bonding in phenolic oligomers is directly reflected in their titration curves and may be responsible for their distinct stepwise neutralization.



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