

# NMR STUDY OF THE PHENOL-FORMALDEHYDE-WATER SYSTEM

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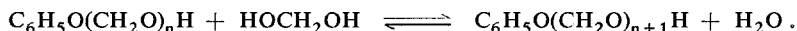
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Equilibrium states of the phenol-formaldehyde-water system were characterised by NMR spectra analysis. It was confirmed that the addition of phenol to water solution of formaldehyde leads to the formation of linear polymers of this type —  $C_6H_5O(CH_2O)_nH$ . Equations for calculating their concentrations were put forward.

While the signal of  $-CH_2-$ protons of linear polymers of the general formula  $CH_3O(CH_2O)_nH$ , formed in water-methanol solution of formaldehyde, is shifted towards higher magnetic field due to the presence of  $CH_3$ -group<sup>1</sup>, the signal of  $-CH_2-$ protons of  $C_6H_5O(CH_2O)_nH$  polymers, prepared by addition of phenol to water solution of formaldehyde, is shifted to lower magnetic field (comp.<sup>2</sup>). As the effect of substituents is an additive one we are able to calculate quite accurately the position of absorption signals by using Shooley's effective shielding constants for given substituents<sup>3</sup>.

In NMR spectra of water solutions of phenol and formaldehyde one can quite distinctly identify up to twelve signals of  $-CH_2-$ protons of the  $HO(CH_2O)_nH$  and  $C_6H_5O(CH_2O)_nH$  polymers; the concentration of which depends on the phenol-formaldehyde molar ratio. Kopf and Wagner<sup>2</sup> have described spectrum of water solution containing 56 mol % of phenol and 13 mol % of formaldehyde and have determined relative equilibrium constants of the process:



The spectrum does not show any other signals which would indicate other reaction products.

The present study evaluates the spectra of the phenol-formaldehyde-water system in which the phenol-formaldehyde molar ratio was ranging from 1 : 15 up to 1 : 0.1. The information presented in this study can be of importance when reviewing a simplified mechanism of phenol-formaldehyde resin formation in acidic and alkaline medium when the existence of  $C_6H_5O(CH_2O)_nH$  polymers in water solutions of phenol and formaldehyde is very often neglected.

## EXPERIMENTAL

<sup>1</sup>H-NMR spectra of water solutions of phenol with formaldehyde were run on a Tesla 487 A apparatus (80 MHz) at 25 and 80°C. Hexamethyldisiloxane in sealed capillary was used as an external standard.

## RESULTS

NMR spectra of water solutions of phenol with formaldehyde consist of two groups of signals due to  $-\text{CH}_2-$  protons of the  $\text{HO}(\text{CH}_2\text{O})_n\text{H}$  (I) and  $\text{C}_6\text{H}_5\text{O}(\text{CH}_2\text{O})_n\text{H}$  (II) linear polymers. The first group of lines at higher magnetic field includes six signals assigned to  $-\text{CH}_2-$  protons of polymer I including the hydrated form of the monomer — hydroxymethanol. The molecular weight of polymer I slightly increases with increasing phenol concentration in water solution of formaldehyde up to the phenol-formaldehyde molar ratio 1 : 2 (pH  $\sim$  4.3). The signals of this group obtained for the initial phenol-formaldehyde molar ratio 1 : 15.01 can be denoted and arranged according to an increasing magnetic field as follows (Fig. 1a):

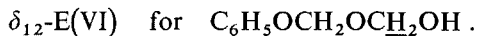
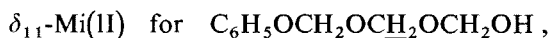
$\delta_1$ -Mi	middle groups	$-\text{O}-\text{CH}_2-\text{O}-$	at $n = 3$ ,
$\delta_2$ -Mi(I)	middle groups	$-\text{O}-\text{CH}_2-\text{O}-$	at $n = 3$ ,
$\delta_3$ -E	end groups	$\text{HO}-\text{CH}_2-\text{O}-$	at $n = 2$ ,
$\delta_4$ -E(I)	end groups	$\text{HO}-\text{CH}_2-\text{O}-$	at $n = 3$ ,
$\delta_5$ -E(II)	end groups	$\text{HO}-\text{CH}_2-\text{O}-$	at $n > 3$ ,
$\delta_6$ -Mo	hydroxymethanol	$\text{HO}-\text{CH}_2-\text{OH}$ .	

Phenol produces the chemical shift changes of vicinal group protons of polymer I. The shift of  $-\text{CH}_2-$  proton signals is towards higher values of  $\delta$  and for polymer I increases starting from the trimer upwards. At the ratio of the components corresponding to the formation of the polymer II the sequence of signals arranged according to an increasing magnetic field is the following: Mi, E, Mi(I), Mo, E(I), E(II) (Fig. 1b). The signals quoted are in the 4.85–5.25 p.p.m. region. At the phenol-formaldehyde molar ratio 1 : 2, the second group of signals appears at around 5.32 p.p.m. It consists of four singlets of methylene protons of polymer II,  $\text{C}_6\text{H}_5\text{OCH}_2\text{O}(\text{CH}_2\text{O})_{n-1}\text{H}$  (Fig. 1c). Their intensity increases with increasing phenol concentration in the system (underlined methylene group corresponds to a given signal). The individual signals were denoted as follows:

$\delta_7$ -E(III)	for $n = 2$ ,
$\delta_8$ -Mo(I)	for $n = 1$ ,
$\delta_9$ -E(IV)	for $n = 3$ ,
$\delta_{10}$ -E(V)	for $n > 3$ .

The appearance of this group of lines is simultaneously followed by the disappearance of Mi, Mi(I), E(I), E(II) signal of the right group. But, in the left part of the right group of lines two new signals appear. These are directly related to E(III) and Mo(I)

signals. They are denoted as



Knowing the molar concentration of  $-\text{CH}_2\text{O}-$  groups in water solution of formaldehyde with phenol,  $c_0$ , we can calculate the molar concentration of hydroxymethanol,  $c_{\text{Mo}}$ , according to

$$c_{\text{Mo}} = I_{\text{Mo}} \cdot R, \quad (1)$$

where  $R$  is an auxiliary magnitude given by

$$R = c_0 / [I_{\text{Mo}} + I_{\text{Mo(I)}} + I_{\text{E}} + I_{\text{E(I)}} + I_{\text{E(II)}} + I_{\text{E(III)}} + I_{\text{E(IV)}} + I_{\text{E(V)}} + I_{\text{E(VI)}} + I_{\text{Mi}} + I_{\text{Mi(I)}} + I_{\text{Mi(II)}}]. \quad (2)$$

$I_{\text{Mo}}$  up to  $I_{\text{Mi(II)}}$  are signal intensities of  $-\text{CH}_2-$  protons of polymers  $I$  and  $II$  in arbitrary units. They were determined from integral records by measuring the heights

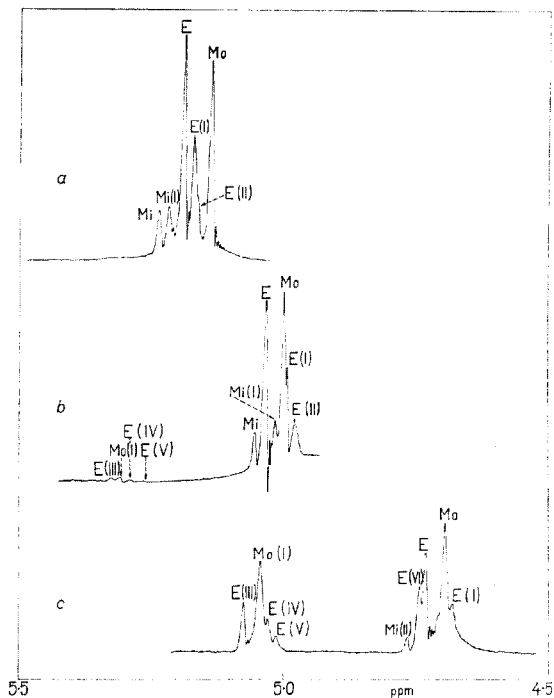


FIG. 1

NMR Spectra (80 MHz) of Water Solutions of Phenol with Formaldehyde (80°C)

Number of mol of formaldehyde per 1 mol of phenol: (a) 15.01, (b) 2.26, (c) 0.226.

of signals and by planimetry. Molar concentration of phenoxymethanol  $c_{\text{Mo(I)}}$  is given by

$$c_{\text{Mo(I)}} = I_{\text{Mo(I)}} \cdot R. \quad (3)$$

Total molar concentration of all components is

$$c = [(I_{\text{Mo}} + I_{\text{Mo(I)}}) + I_{\text{E}} + I_{\text{E(I)}} + I_{\text{E(II)}} + I_{\text{E(III)}} + I_{\text{E(VI)}/2}] + I_{\text{E(IV)}} + I_{\text{E(V)}}] \cdot R \quad (4)$$

It is a summ of molar concentration of the polymer *I*,  $c_I$  and polymer *II*,  $c_{II}$ :

$$c_I = [I_{\text{Mo}} + (I_{\text{E}} + I_{\text{E(I)}} + I_{\text{E(II)}}/2)] \cdot R \quad (5)$$

$$c_{II} = [I_{\text{Mo(I)}} + (I_{\text{E(III)}} + I_{\text{E(VI)}/2}) + I_{\text{E(IV)}} + I_{\text{E(V)}}] \cdot R. \quad (6)$$

Signal intensity of  $-\text{CH}_2-$ protons of the polymer *II*,  $\text{C}_6\text{H}_5\text{OCH}_2\text{O}(\text{CH}_2\text{O})_{n-1}\text{H}$ , for  $n = 4$  is so small that it can not substantially influence the value of  $c_I$  and therefore polymer *II* can be regarded as a mixture of mono-, di- and trimers. Molar

TABLE I

Summarised Data on Formaldehyde-Phenol-Water Solutions

$c_f$  Formaldehyde concentration in water solution of phenol expressed in wt. %. For other symbols see the text.

<i>F</i>	$c_f$	$c_0$	$c_{\text{Mo}}$	$c$	$c_I$	$c_{II}$	$c_{\text{Mo(I)}}$	$c_d$	$c_p$
$\infty^a$	36.10	13.390	3.92	7.48	7.48	—	—	—	—
15.01	33.60	12.404	3.61	6.92	6.92	—	—	—	—
7.52	31.40	11.560	3.56	6.67	6.67	—	—	—	—
4.51	28.88	10.615	3.35	6.47	6.47	—	—	—	—
2.26	24.08	8.800	2.50	5.05	4.68	0.37	0.19	0.10	0.01
1.13	18.05	6.567	1.87	4.21	3.63	0.58	0.30	0.15	0.13
0.564	12.03	4.343	1.21	2.88	2.17	0.71	0.38	0.18	0.15
0.376	9.03	3.257	0.868	2.23	1.41	0.82	0.46	0.20	0.16
0.282	7.22	2.603	0.706	1.96	1.06	0.90	0.51	0.22	0.16
0.226	6.02	2.168	0.574	1.65	0.79	0.86	0.52	0.21	0.13
0.188	5.16	1.856	0.475	1.40	0.59	0.81	0.52	0.20	0.09
0.161	4.21	1.622	0.405	1.28	0.53	0.75	0.52	0.15	0.07
0.113	3.28	1.178	0.258	0.96	0.30	0.66	0.53	0.13	—

<sup>a</sup> Water solution of formaldehyde.

concentration of 3-phenoxy-2-oxapropanol,  $c_d$ , is given by

$$c_d = [I_{E(III)} + I_{E(VI)}/2] \cdot R. \quad (7)$$

Molar concentration of polymer *II* having  $n > 2$ ,  $c_p$ , can be calculated from

$$c_p = c_{II} - (c_{Mo(I)} + c_d). \quad (8)$$

The resulting values are summarised in Table I.

Because of the variable concentration of  $-\text{CH}_2\text{O}-$  groups in measured solution it is suitable to determine the relative polymer *II* concentration in water solutions of formaldehyde with phenol.

$$\alpha = c_{II}/c. \quad (9)$$

The relative proportions of phenoxymethanol, 3-phenoxy-2-oxapropanol and polymer *II* having  $n > 2$  in the total mass of polymer *II* are given by

$$\beta = c_{Mo(I)}/c_{II}, \quad \beta' = c_d/c_{II}, \quad \beta'' = c_p/c_{II}. \quad (10-12)$$

For different formaldehyde/phenol molar ratios,  $F$ , the following values were found:

$F$ :	2.26	1.13	0.564	0.376	0.282	0.226	0.188	0.161	0.153
$\alpha$ :	7.3	13.6	24.5	36.8	45.9	52.1	57.8	58.5	68.5
$\beta$ :	51.1	51.6	53.2	55.1	57.1	60.3	64.3	70.0	80.6
$\beta'$ :	25.9	25.8	25.3	25.2	25.0	25.0	24.4	20.7	19.4
$\beta''$ :	22.6	22.6	21.5	19.7	17.9	14.7	11.3	9.3	—

The measurements of *o*- and *p*-methylolphenols spectra rules out the possibility of such compounds formation under the given conditions without the presence of a catalyst. Also the formation of cyclic compounds such as cyclo-1,3,5-trioxahexane in the phenol-formaldehyde-water systems does not take place.

#### REFERENCES

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