

## 77. Acidities of Hydrochloric Acid in Water/Acetic Acid and in Water/Acetic Acid/Formaldehyde Mixtures: Investigations with the Indicator Method and with the NMR Method

31st Communication on investigations in textile chemistry<sup>1)</sup>.

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*Summary.* The NMR. chemical shift ( $\delta_H$ ) of the acidic proton in the systems HCl/H<sub>2</sub>O and HCl/H<sub>2</sub>O/HOAc was correlated with the acidity function ( $H_o$ )<sub>I</sub> determined by the indicator method. By using three indicators it could be shown that, except for solutions with very low concentrations of hydrochloric acid, the acidity function ( $H_o$ )<sub>I</sub> correlates with  $\delta_H$  in a way which can be rationalized. Addition of 7,5% (W) formaldehyde to these systems changes ( $H_o$ )<sub>I</sub> and  $\delta_H$  very significantly, particularly in systems with low water content. Logarithmic rate constants of cellulose formal formation in HCl/H<sub>2</sub>O/HOAc systems which do not show a linear relationship with ( $H_o$ )<sub>I</sub>, measured without presence of formaldehyde, do so if ( $H_o$ )<sub>I</sub> is measured with formaldehyde present. For these systems, however,  $\delta_H$  is not a suitable acidity parameter.

**1. Introduction.** – We are interested in the acidities of mineral acids in various water/acetic acid/formaldehyde systems because they are used as media for cross-linking cellulose, particularly in cotton fabrics [2] [3]. We showed that the overall process is complex and, depending on reaction conditions, different partial processes may become rate-limiting [2]. These partial processes may be of a physical nature, namely swelling of cellulose (*i.e.* diffusion of the solvent into the polymer), diffusion and physisorption of the reactants and the catalyst into the fibre, or they may be chemical reactions, namely formation of cellulose hemiformals (Cell-OCH<sub>2</sub>OH), grafting of these formals (Cell-O-(CH<sub>2</sub>O)<sub>n</sub>-H) and formal formation, *i.e.* crosslinking proper of the hemiformals and the grafted hemiformals (Cell-O-(CH<sub>2</sub>O-)<sub>n</sub>-Cell').

Under our reaction conditions the formal formation is catalyzed by mineral acids<sup>2)</sup>.

In a previous paper [3] we demonstrated for water/hydrochloric acid systems that the logarithms of the rate of formal formation are proportional to the negative values of *Hammitt's* acidity function,  $H_o$ .

$H_o$ , as defined by equation (2) and determined by *Hammitt's* indicator method [4] through equation (3) is a measure of proton activity provided the ratio of activity coefficients in (1) and (2) is equal to one; this is an assumption which, however, cannot be directly tested.

$$K_{BH^{\oplus}} = a_H^{\oplus} \frac{[B] \gamma_B}{[BH^{\oplus}] \gamma_{BH^{\oplus}}} \quad (1)^3$$

$$H_o = -\log a_H^{\oplus} - \log (\gamma_B / \gamma_{BH^{\oplus}}) \quad (2)$$

$$H_o = pK_{BH^{\oplus}} - \log ([BH^{\oplus}] / [B]) \quad (3)$$

<sup>1)</sup> 30th communication of this series: *U. Meyer* [1].

<sup>2)</sup> Acid catalysis of the hemiformal formation is also in principle to be expected too; yet, we did not investigate it in this research project.

<sup>3)</sup>  $K_{BH^{\oplus}}$ : equilibrium constant for the indicator acid/base equilibrium  $B + H^{\oplus} \rightleftharpoons BH^{\oplus}$ .  
 $a_H^{\oplus}$ : proton activity;  $\gamma$ : activity coefficients.

In addition, experience [5a] has shown that the validity of  $H_0$  values in mixed solvents, such as those used for our crosslinking reactions, may be questionable for a variety of reasons, particularly if  $pK_{BH^*}$  values for the indicator are assumed to be the same as they are in water [6].

When we investigated the rate of formal formation in aqueous hydrochloric acid [3a], we found a linear relation between the logarithms of reaction rates with  $-H_0$ , but not in solutions containing 4.41M HCl with varying  $H_2O/HOAc$  ratio. Because the acidity functions of these mixtures were measured in absence of formaldehyde, we decided to investigate not only these systems with formaldehyde present, but also to determine if, instead of the indicator method of *Hammitt*, NMR. chemical shifts could be used in mixed solvents. *Zarakhani & Vinnik* [7] compared chemical shifts ( $\delta_H$ ) of aqueous solutions of various mineral acids to  $H_0$  values and found them linearly related, thereby suggesting  $\delta_H$  as a measure of the activity of solvated protons. Their work indicated, however, a difficulty, namely the slope and intercept of the  $\delta_H/H_0$  relationship depended on the anion of the acid used.

It is therefore the purpose of this investigation to determine acidity functions by the indicator method,  $(H_0)_I$  and  $\delta_H$  values for HCl/ $H_2O$ /HOAc solutions and to discuss the relationship between these two parameters. Furthermore  $(H_0)_I$  will be determined in HCl/ $H_2O$ /HOAc/ $CH_2O$  systems.

There are various methods to determine acidity functions giving numerically different values for  $H_0$ . Therefore we indicate  $H_0$  values determined by the indicator method by the respective index:  $(H_0)_I$ .

**2. Experimental.** – While deionized  $H_2O$  was distilled from basic permanganate, *Merck* (*pro analysi*) HOAc (100%) and 37% HCl solutions were used with no further purification. Solution compositions ( $\pm 0,7\%$  – by weight) are given in Tables 1 and 2.

A *Varian* A60-T spectrometer was used to obtain NMR. spectra with DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as the internal standard and  $\delta_H$  values are accurate to  $\pm 0.03$  ppm.

*p*-Nitroaniline, *o*-nitroaniline and 4-chloro-2-nitroaniline were obtained from *Merck*, *Merck & Schuchardt*, Munich, respectively, and were purified by recrystallization from EtOH/ $H_2O$  until their m.p. agreed with literature values. Stock solutions of each indicator in HOAc were prepared.

A *Beckman* Acta II spectrophotometer and one cm quartz cells, each holding 3 ml of solution, were used to obtain  $\epsilon$  values for the indicators. While  $\epsilon_B$  values were redetermined prior to each analysis, average  $\epsilon$ 's based on at least two determinations were used to obtain  $\log ([BH^+]/[B])$  values. When the amount of stock solution introduced was greater than 0.01 ml, a volume correction was made<sup>4)</sup>. Absorption measurements were made at the wavelengths given below.  $\epsilon_{BH^*}$  for *p*-nitroaniline is the value suggested by *Salomaa* [8]:

	in AcOH	in acidic solutions
<i>p</i> -Nitroaniline ( $\epsilon_{BH^*} = 60$ )	358 nm	382 nm
<i>o</i> -Nitroaniline ( $\epsilon_{BH^*} = 0$ )	400 nm	409 nm
4-Chloro-2-nitroaniline ( $\epsilon_{BH^*} = 0$ )	410 nm	425 nm

$[BH^+]/[B]$  was calculated with the molar extinction coefficients of the buffer acid ( $\epsilon_{BH^*}$ ) given in brackets.

For the solutions containing formaldehyde, we considered the possibility of formaldehyde reacting with the indicator base, at the anion group or even at the benzene ring, forming not only N- and C-methylol compounds, but also N,N', 2,2'- or 4,4'-diarylaminomethylene compounds.

<sup>4)</sup> For further details see also [3].

Table 1. *Composition of solutions (weight percent) without formaldehyde present*

Solution No.	HCl (100%)	H <sub>2</sub> O	HOAc	Solution No.	HCl (100%)	H <sub>2</sub> O	HOAc
1	0	100	–	23	0	50	50
2	2.1	97.9	–	24	2.1	50	47.9
3	4.3	95.7	–	25	4.3	50	45.7
4	6.2	93.8	–	26	6.3	50	43.7
5	8.2	91.8	–	27	8.2	50	41.7
6	10.5	89.5	–	28	10.5	50	39.5
7	14.5	85.5	–	29	0	70	30
8	19.1	80.9	–	30	2.1	70	27.9
9	25.1	74.8	–	31	4.3	70	25.7
10	0	23.5	76.5	32	6.3	70	23.7
11	2.1	23.5	74.4	33	8.2	70	21.7
12	4.3	23.5	72.2	34	10.5	70	19.5
13	6.2	23.5	70.3	35	0	80	20
14	8.2	23.5	68.3	36	2.1	80	17.9
15	10.5	23.5	66.0	37	4.3	80	15.7
16	13.8	23.5	62.7	38	6.3	80	13.7
17	0	40	60	39	8.2	80	11.7
18	2.1	40	57.9	40	10.5	80	9.5
19	4.3	40	55.7	41	14.5	85	0.5
20	6.2	40	53.7	42	14.5	80	5.5
21	8.2	40	51.7	43	14.5	70	15.5
22	10.5	40	49.5	44	14.5	60	25.5
				45	14.5	50	35.5
				46	14.5	40	45.5
				47	14.5	30	55.5
				48	14.5	25	60.5
				49	14.5	18	67.5

Table 2. *Composition of solutions with formaldehyde present (R = Rest to 100 ml)*

Solution No.	Paraformaldehyde g/100 ml	HCl (100%) g/100 ml	H <sub>2</sub> O g/100 ml	HOAc g/100 ml
50	7.5	5	R	–
51	7.5	12	R	–
52	7.5	15	R	–
53	7.5	18	R	–
54	7.5	20	R	–
55	7.5	22	R	–
56	7.5	17.5	20	R
57	7.5	17.5	30	R
58	7.5	17.5	40	R
59	7.5	17.5	50	R
60	7.5	17.5	60	R
61	7.5	17.5	70	R

Formation of such compounds would of course complicate the use of these aniline derivatives mentioned as indicators. We compared therefore the spectra of solutions in given water/acetic acid mixtures containing one of the indicators, hydrochloric acid and formaldehyde with the respective solutions without formaldehyde but with such a hydrochloric acid concentration that the same or almost the same  $\epsilon_B$  was obtained for both solutions. The shape of the whole UV. spectrum was compared and found to be identical within experimental limits. We conclude therefore that the equilibrium concentration of these addition products of formaldehyde to these amines is very small and can be neglected<sup>5)</sup>.

Table 3 contains the measured  $\log ([BH^+]/[B])$  values for the hydrochloric acid solutions mentioned in Tables 1 and 2, using the three indicators (*p*-nitroaniline, *o*-nitroaniline and 4-chloro-2-nitroaniline). Indicator concentrations were 0,0253-0,0258 M, T = 25°C.

Table 3. Indicator acid/base ratio measured

Solution No.	$\log ([BH^+]/[B])$			Solution No.	$\log ([BH^+]/[B])$		
	<i>p</i> -nitroaniline	<i>o</i> -nitroaniline	4-chloro-2-nitroaniline		<i>p</i> -nitroaniline	<i>o</i> -nitroaniline	4-chloro-2-nitroaniline
1	-1.12	-	-1.00	29	-1.58	-1.00	-
2	0.98	-	-0.82	30	+0.72	-0.50	-
3	1.38	-	-0.55	31	+1.19	-0.11	-
4	1.67	0.41	-0.31	32	-	+0.16	-
5	-	0.61	-0.11	33	-	+0.44	-
6	-	0.88	+0.10	34	-	+0.76	-
7	-	1.29	+0.52	35	-1.25	-1.01	-
8	-	1.87	+1.11	36	+0.76	-0.44	-
9	-	-	+1.78	37	+1.21	-0.10	-
10	-1.29	-1.41	-1.35	38	-	+0.20	-
11	+1.33	-0.13	-0.88	39	-	+0.47	-
12	+1.81	+0.56	-0.31	40	-	+0.75	-
13	-	+1.00	+0.17	41	-	+1.26	+0.49
14	-	+1.57	+0.67	42	-	+1.25	+0.46
15	-	-	+1.12	43	-	+1.29	+0.49
16	-	-	+1.64	44	-	+1.38	+0.58
17	-0.86	-1.30	-	45	-	+1.42	+0.75
18	+0.91	-0.45	-	46	-	-	+1.05
19	+1.49	+0.04	-	47	-	-	+1.42
20	-	+0.45	-	48	-	-	+1.59
21	-	+0.76	-	49	-	-	+2.00
22	-	+1.20	-	50	-	-	-1.11
23	-1.42	-1.19	-	51	-	-	-0.66
24	+0.79	-0.58	-	52	-	-	-0.47
25	+1.31	-0.08	-	53	-	-	-0.24
26	-	+0.21	-	54	-	-	-0.07
27	-	+0.56	-	55	-	-	+0.08
28	-	+0.92	-	56	-	-	-0.34
				57	-	-	-0.23
				58	-	-	-0.16
				59	-	-	-0.20
				60	-	-	-0.27
				61	-	-	-0.34

<sup>5)</sup> We thank Mr. H. P. Knecht (ETHZ) for these measurements.

**3. Results and Discussion.** – 3. 1. *Acidity Functions in the System Hydrochloric Acid/Water/Acetic Acid.* Based on the spectrophotometric measurements of the acid/base equilibria of indicators used (*p*-nitroaniline, *o*-nitroaniline and 4-chloro-2-nitroaniline) the logarithmic ratios  $[BH^{\oplus}]/[B]$  are plotted in Fig. 1 and 2 as a function of hydrochloric acid concentration for the purely aqueous systems and for the system containing 23.5%  $H_2O$ . In Fig. 3  $\log ([BH^{\oplus}]/[B])$  of 14.5% HCl in mixtures of various water/acetic acid ratios are plotted against the water content of the systems.

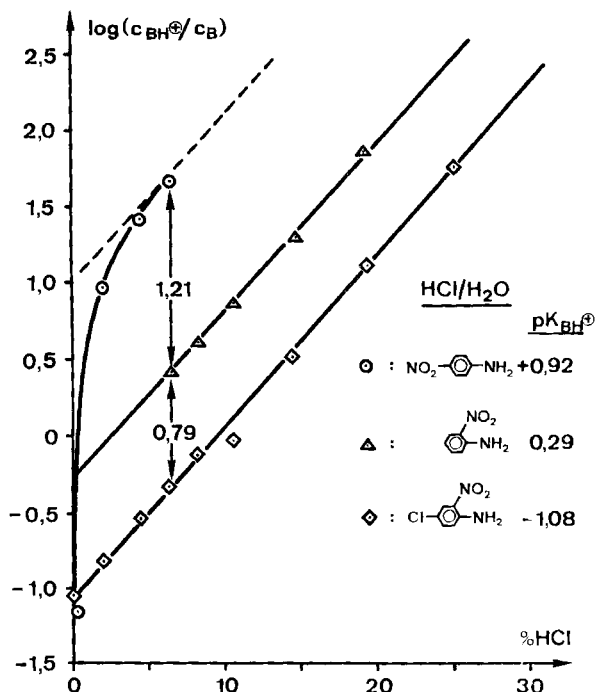


Fig. 1. Acid/base indicator ratios in 2.1 to 25.1% HCl in  $H_2O$  (Solutions 2–9)

The method which Růček [6] suggested for the evaluation of acidities in solvents other than water, can be applied to the data of Fig. 1–3: The  $pK_{BH^{\oplus}}$  values for the indicators used are related to a standard indicator I whose  $pK_{BH^{\oplus}}$  is assumed to be the same as it is in water. The following equations are used:

$$(H_0)_I = (pK_{BH^{\oplus}})_I - \log ([BH^{\oplus}]/[B]) \quad (4)$$

$$(pK_{BH^{\oplus}})_I = \log ([BH^{\oplus}]/[B]) - \log ([IH^{\oplus}]/[I]) + pK_{IH^{\oplus}}^Y \quad (5)$$

In (5)  $pK_{IH^{\oplus}}^Y$  is the value for the standard indicator in water. It is clear from (4) and (5) that in plots of  $\log ([BH^{\oplus}]/[B])$  versus the appropriate concentration of one of the components in the solution, the difference between the standard indicator curve and the curve of another indicator can be used in (5) at a point where the two curves are parallel. Examples of such evaluations have been previously used, e.g. by Wáhlowský & Chválowský [9].

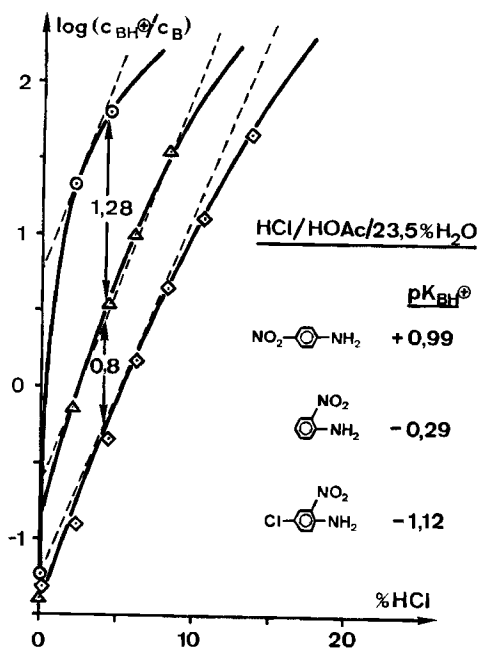


Fig. 2. Acid/base indicator ratios in 2.1 to 13.8% HCl + 23.5% H<sub>2</sub>O + rest HOAc (Solutions 11-16)

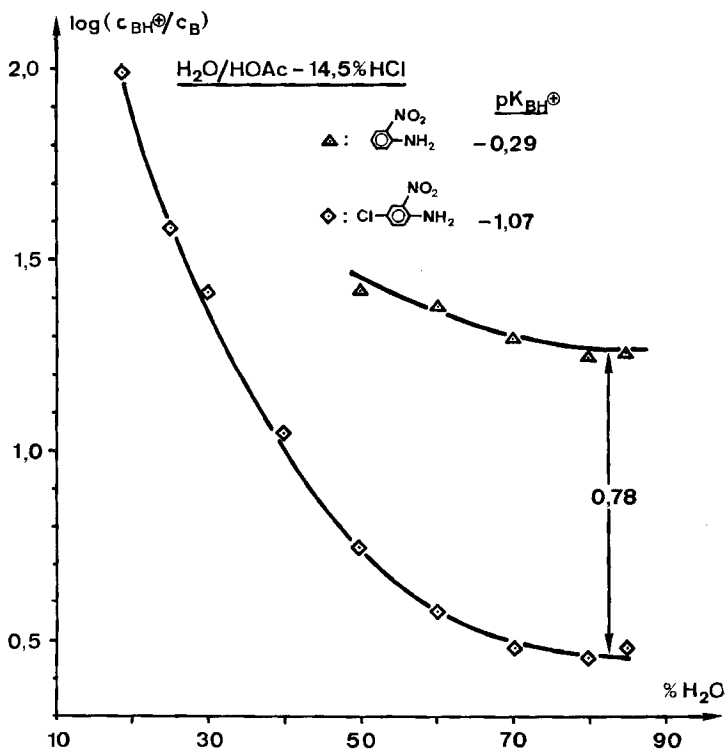


Fig. 3. Acid/base indicator ratios of 14.5% HCl in 85 to 18% H<sub>2</sub>O + rest HOAc (Solutions 41-49)

Using *o*-nitroaniline as the standard indicator, application of this technique to our systems yielded the  $pK_{BH^{\oplus}}$  values given in Table 4 and the  $(H_0)_I$  values of Table 5.

Table 4.  $pK_{BH^{\oplus}}$  values used for this investigation

Indicator	$pK_{BH^{\oplus}}$			
	Lit. [5b] HCl/H <sub>2</sub> O	HCl/H <sub>2</sub> O	HCl/HOAc/ 23.5% H <sub>2</sub> O	H <sub>2</sub> O/HOAc/ 14.5% HCl
<i>o</i> -nitroaniline	-0.29	-0.29 <sup>a)</sup>	-0.29 <sup>a)</sup>	-0.29 <sup>a)</sup>
<i>p</i> -nitroaniline	+0.99	+0.92	-0.99	-
4-chloro-2-nitroaniline	-1.03	-1.08	-1.12	-1.07

<sup>a)</sup> Standard

Table 5.  $(H_0)_I$  values and chemical shifts ( $\delta_H$ ) for various indicators in HCl/H<sub>2</sub>O/HOAc systems

Solution No. <sup>a)</sup>	$(H_0)_I$			$\delta_H^b)$
	<i>p</i> -nitroaniline	<i>o</i> -nitroaniline	4-chloro-2- nitroaniline	ppm
1	+2.04	-	-	4.64
2	-0.06	-	-0.26	4.86
3	-0.46	-	-0.53	5.02
4	-0.73	-0.70	-0.77	5.21
5	-	-0.90	-0.97	5.42
6	-	-1.17	-1.18	5.62
7	-	-1.58	-1.60	5.94
8	-	-2.16	-2.19	6.46
9	-	-	-2.89	7.15
10	+0.23	-	-	6.86
11	-0.34	-0.16	-0.24	7.19
12	-0.82	-0.85	-0.81	7.65
13	-	-1.35	-1.29	8.03
14	-	-1.86	-1.79	8.30
15	-	-	-2.24	8.74
16	-	-	-2.76	9.16
17	+1.85	+1.01	-	5.91
18	+0.08	+0.16	-	6.26
19	-0.50	-0.33	-	6.52
20	-	-0.74	-	6.77
21	-	-1.05	-	7.05
22	-	-1.49	-	7.35
23	+2.41	+0.90	-	5.57
24	+0.20	+0.29	-	5.75
25	-0.32	-0.21	-	6.17
26	-	-0.50	-	6.27
27	-	-0.85	-	6.58
28	-	-1.21	-	6.84

Solution No. <sup>a)</sup>	$(H_0)_I$			$\delta_H^b)$ ppm
	<i>p</i> -nitroaniline	<i>o</i> -nitroaniline	4-chloro-2-nitroaniline	
29	+2.57	+0.71	-	5.11
30	+0.27	+0.21	-	5.32
31	-0.20	-0.18	-	5.56
32	-	-0.45	-	5.75
33	-	-0.73	-	5.98
34	-	-1.05	-	6.12
35	+2.04	+0.72	-	4.94
36	+0.23	+0.15	-	5.15
37	-0.22	-0.19	-	5.33
38	-	-0.49	-	5.51
39	-	-0.76	-	5.66
40	-	-1.04	-	5.85
41	-	-1.55	-1.56	6.04
42	-	-1.54	-1.53	6.18
43	-	-1.58	-1.56	6.52
44	-	-1.67	-1.65	6.90
45	-	-1.71	-1.82	7.34
46	-	-	-2.12	7.92
47	-	-	-2.49	8.71
48	-	-	-2.66	9.16
49	-	-	-3.02	9.78

- a) No. 1-9 : 0 to 25.1% HCl in H<sub>2</sub>O  
 No. 10-16 : 0 to 13.8% HCl + 23.5% H<sub>2</sub>O, rest HOAc  
 No. 17-22 : 0 to 10.5% HCl + 40% H<sub>2</sub>O, rest HOAc  
 No. 23-28 : 0 to 10.5% HCl + 50% H<sub>2</sub>O, rest HOAc  
 No. 29-34 : 0 to 10.5% HCl + 70% H<sub>2</sub>O, rest HOAc  
 No. 35-40 : 0 to 10.5% HCl + 80% H<sub>2</sub>O, rest HOAc  
 No. 41-49 : 14.5% HCl, 85 to 18% H<sub>2</sub>O, rest HOAc (see Table 1).

b) 60 MHz, DSS as internal standard.

As can be seen from Table 4, the acidities of the indicators in these solutions compare favourably with the literature values. Therefore, the assumption that these indicators are behaving in mixed solvents similarly as in water, while now reasonable, was previously unconfirmed.  $(pK_{BH^{\oplus}})_I$  values were used to determine  $(H_0)_I$  values to be internally consistent (Table 5).

Table 5 contains also the chemical shifts ( $\delta_H$ ) of these solutions. These  $\delta_H$  values are plotted as a function of  $(H_0)_I$  in Fig. 4. This figure indicates that  $(H_0)_I$  and  $\delta_H$  are linearly related for the various acidic solutions investigated. The correlation coefficients (Table 6) are excellent. The slopes of the HCl/H<sub>2</sub>O and HCl/HOAc - 23.5% H<sub>2</sub>O solution lines are essentially the same while the H<sub>2</sub>O/HOAc/14.5% HCl solution line is considerably different. Although the H<sub>2</sub>O/HOAc/14.5% HCl and HCl/HOAc/-23.5% H<sub>2</sub>O solution lines cross at approximately that solution composition which is common to both, the H<sub>2</sub>O/HOAc/14.5% HCl solution line does not intersect the HCl/H<sub>2</sub>O solution line at 14.5% HCl/H<sub>2</sub>O but at a lower percentage of HCl. To determine whether this anomaly was real, solutions with low concentrations of



HOAc (0.5 and 5.5%) in 14.5% HCl/H<sub>2</sub>O were studied. It was found that while  $\delta_H$  varied, the  $(H_o)_I$  values were essentially the same when the amount of HOAc varied from 0 to 15.5% for these solutions. The acidic protons for low concentrations of HOAc in these solutions must be essentially residing on water molecules, which are surrounded by a H<sub>2</sub>O solvent shell, thereby indicating that H<sub>2</sub>O is the strongest base present as already found for HCl/H<sub>2</sub>O/HOAc systems by *Schwarzenbach et al.* [10]. As the amount of water decreases by replacing it with HOAc (an ion pair forming solvent) the indicator present then becomes the strongest base and hence it becomes more protonated as indicated by the varying  $(H_o)_I$  values obtained. This problem is not observed in the NMR. spectra of these solutions since the indicators are absent. This is definitely an advantage of the NMR. acidity function scale, while the dependence on anion structure of the mineral acid used, as observed by *Zarakhani & Vinnik* [7] is a disadvantage.

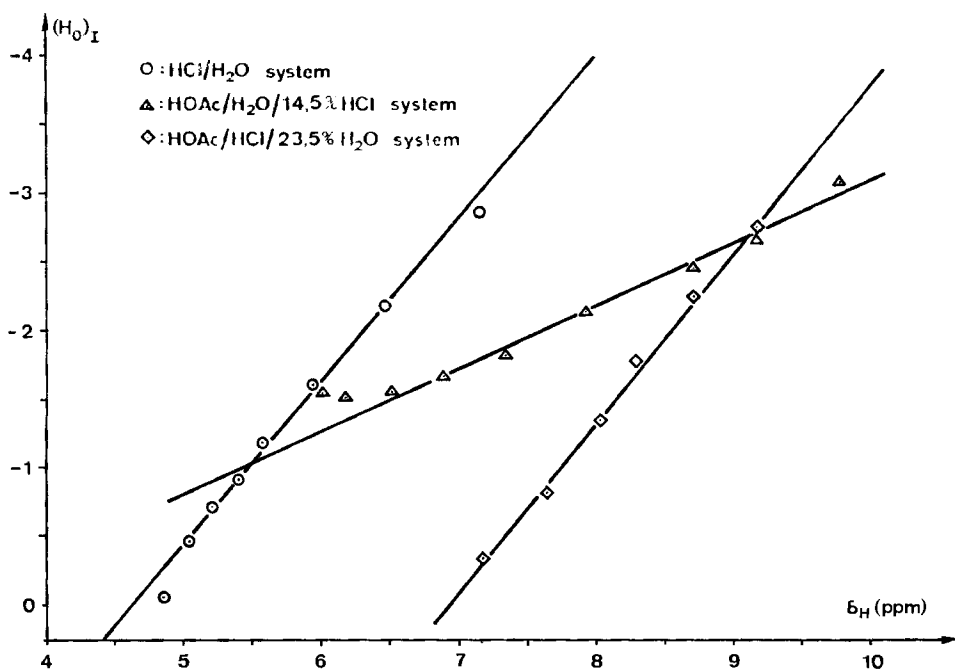


Fig. 4.  $\delta_H$  as a function of  $(H_o)_I$  in HCl/H<sub>2</sub>O/HOAc systems

Based on the correlations found for the three series of solutions discussed above, the other series were evaluated in the same way. The results are also included in Tables 5 and 6. The series with 40%, 50%, 70% and 80% water contain weakly acidic solutions. As can be seen, the agreement between  $(H_o)_I$  values is good except for the solutions which do not contain HCl. The lack of agreement between  $(H_o)_I$  values obtained from different indicators for these solutions is expected because of the errors in the  $(H_o)_I$  acidity determination method for very weak acidic solutions. This demonstrates clearly the linear and the nonlinear parts of the relationship

Table 6. Least square correlations between  $(H_o)_I$  and  $\delta_H$  for acidic solutions (Fig. 4)  
 $x = \delta_H$ ;  $y = (H_o)_I^a$

Solutions <sup>b)</sup>	Slope	Intercept	Correlation coefficient r
	a	b	
HCl/H <sub>2</sub> O	-1.21	5.64	0.998
HCl/80% H <sub>2</sub> O/HOAc	-1.57	8.18	0.999
HCl/70% H <sub>2</sub> O/HOAc	-1.46	7.92	0.997
HCl/50% H <sub>2</sub> O/HOAc	-1.33	7.88	0.996
HCl/40% H <sub>2</sub> O/HOAc	-1.27	7.89	0.998
HCl/23.5% H <sub>2</sub> O/HOAc	-1.25	8.68	0.998
14.5% HCl/H <sub>2</sub> O/HOAc	-0.46	1.53	0.996

a)  $y = ax + b$

b) 2.1% HCl solutions omitted from these calculations for all solutions.

between  $(H_o)_I$  and  $\delta_H$  for all mixtures of systems containing 2.1 to 14.5% HCl, 18 to 98% H<sub>2</sub>O (*i.e.* to purely aqueous hydrochloric acid and 0 to 67.5% HOAc. Also given in Fig. 5 are the  $(H_o)_I$  and the  $\delta_H$  values for H<sub>2</sub>O/HOAc mixture without HCl; they were in part taken from literature [11], in part from our own work.

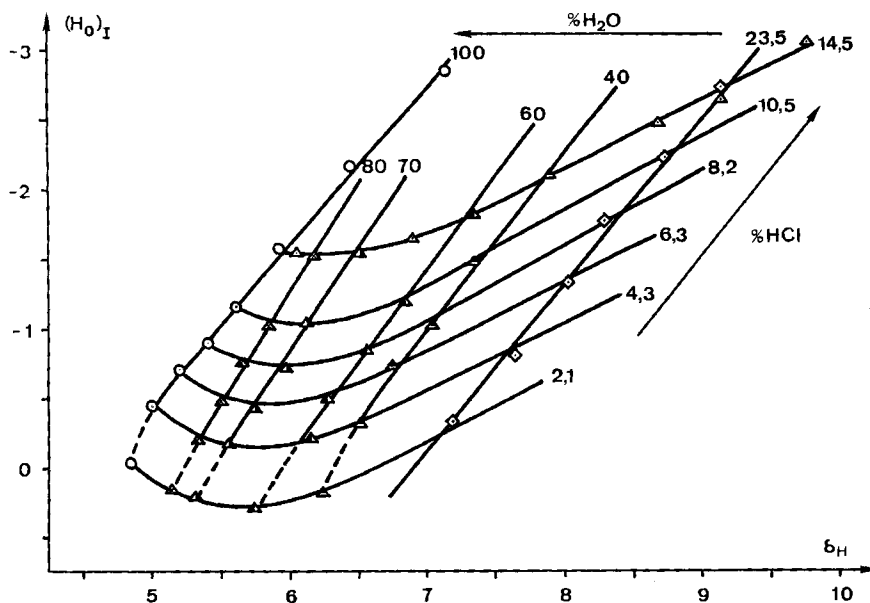


Fig. 5. Correlation between  $(H_o)_I$  and  $\delta_H$  for all HCl|H<sub>2</sub>O|HOAc systems investigated

Although relationships between  $(H_o)_I$  and  $\delta_H$  exist they are not simple. They are apparently linear in the range of hydrochloric acid concentrations  $\geq 4.3\%$ . A fairly smooth change in slope is observable for HCl solutions in H<sub>2</sub>O/HOAc mixtures

containing 23.5 to 80% of water. Yet the slope found for solutions in water only does not correspond with the slope expected from an extrapolation of the slopes for H<sub>2</sub>O/HOAc mixtures with increasing water content. Also, as can be seen from the Figure, minima are obtained for constant HCl lines.

There are, therefore, relationships between  $(H_o)_I$  and  $\delta_H$ , but they are not simple. Yet, as they are apparently linear for the range of acidities of interest, the acidities of solutions can be evaluated with either  $(H_o)_I$  or  $\delta_H$ .

3.2. *Acidity Functions in Presence of Formaldehyde and Rates of Cellulose Formal Formation in HCl/H<sub>2</sub>O/HOAc Systems.* Table 7 contains the  $(H_o)_I$  values and the chemical shifts  $\delta_H$  for aqueous hydrochloric acid and HCl/H<sub>2</sub>O/HOAc systems containing formaldehyde together with the  $(H_o)_I$  values assumed from measurements of solution without formaldehyde. As can be seen from this Table, the agreement between the  $(H_o)_I$  with and without formaldehyde values is poor. In the case of solutions No. 50 to 55 (no HOAc present), the values appear to be off by one  $(H_o)_I$  unit, while the acidities of the solutions containing HOAc are experimentally found to be weaker than predicted. There is a good linear correlation between  $(H_o)_I$  and  $\delta_H$  for the aqueous solutions (no. 50–55): Using the definitions of Table 6, least square regression gives a slope (a) of  $-1.284$ , an intercept (b) of  $5.354$  and a correlation coefficient (r) of  $0.998$ . For solutions containing 17.5% HCl and varying ratios of water and acetic acid, no reasonable correlation exists ( $a = 2.65$ ,  $b = 10.07$ ,  $r = 0.197$ ): Table 7 demonstrates that  $(H_o)_I$  passes a weak minimum where the ratio H<sub>2</sub>O/HOAc is increased, whereas the chemical shift  $\delta_H$  increases steadily with the increase in the water percentage of the system.

In the last column of Table 7 acidity functions for systems with and without formaldehyde are compared: In all cases, addition of formaldehyde decreases the

Table 7. *Acidity functions and chemical shifts in HCl/H<sub>2</sub>O and HCl/H<sub>2</sub>O/HOAc systems containing formaldehyde*

Solution <sup>a)</sup> No.	$(H_o)_I$ <sup>b)</sup> (with CH <sub>2</sub> O)	$\delta_H$	$(H_o)_I$ <sup>c)</sup> (without CH <sub>2</sub> O)	$\Delta$ <sup>d)</sup>
50	+ 0.08	5.21	- 0.47	+ 0.55
51	- 0.37	5.86	- 1.15	+ 0.78
52	- 0.56	6.12	- 1.44	+ 0.88
53	- 0.79	6.38	- 1.73	+ 0.94
54	- 0.96	6.57	- 1.93	+ 0.97
55	- 1.11	6.75	- 2.12	+ 1.01
56	- 0.69	6.80	- 3.21	+ 2.52
57	- 0.80	7.19	- 2.98	+ 2.18
58	- 0.87	7.64	- 2.61	+ 1.74
59	- 0.83	8.22	- 2.30	+ 1.47
60	- 0.76	8.83	- 2.03	+ 1.27
61	- 0.69	9.41	- 2.02	+ 1.23

<sup>a)</sup> No. 50–55: 7.5% paraformaldehyde, 5 to 22% HCl, rest water (see Table 1).

No. 56–61: 7.5% paraformaldehyde, 17.5% HCl, 20 to 70% water, rest acetic acid (see Table 1).

<sup>b)</sup> Based on  $pK_{BH^+} = -1.03$  for 4-chloro-2-nitroaniline (see Table 4).

<sup>c)</sup> Values for solutions no. 50–55 from ref. [5c].

<sup>d)</sup>  $\Delta = (H_o)_I$  (with CH<sub>2</sub>O) -  $(H_o)_I$  (without CH<sub>2</sub>O).

protonating power of the system. The data indicate that this effect is correlated in some way with the water content: In the first series (solutions no. 50 to 55) the water content decreases from 87.5% to 70.5% due to the increase of the concentration of HCl; in the second series the water content increases from 20% (solution no. 56) to 70% (no. 61) with an inverse change of acetic acid content at a constant percentage concentration of HCl (17.5%).

At the present time, only speculations seem to be possible on the causes of that tremendous influence of formaldehyde on acidity functions. As shown in a previous communication [12], formaldehyde is involved in a multiplicity of complex addition and oligomerisation equilibria in systems containing water, acetic acid and hydrochloric acid. Potentially it could be concluded from the relation between the  $\Delta$  values of Table 7 and the water content that water molecules are used for methylene glycol formation ( $\text{HOCH}_2\text{OH}$ ) from  $\text{CH}_2\text{O}$  and paraformaldehyde [ $\text{HO}-(\text{CH}_2-\text{O})_n-\text{H}$ ]. This conclusion is, however, not substantiated by the investigation mentioned [12]: There it was shown that methylene glycol formation decreases with lower water contents of the systems used.

It may be that methylene glycol or other equilibrium products of formaldehyde in these systems are more effective proton acceptors than water.

If this is indeed the case, then  $\delta_{\text{H}}$  values are probably not useful parameters for the protonating power, *i.e.* for the acidity function: The chemical shift is dependent not only on the concentration, but also on the type of proton acceptor. It is only useful if proton transfer between hydroxonium ion and proton acceptors other than water molecules can be neglected.

Therefore, it became even more interesting than anticipated and discussed briefly in the introduction of this investigation, to compare  $(\text{H}_0)_{\text{I}}$  and  $\delta_{\text{H}}$  (measured in presence of  $\text{CH}_2\text{O}$ ) with our previous measurements of the rate of formal formation of cellulose [3].

Using the rate constants  $k_{\text{ex}}$  determined for formal formation in aqueous systems in the previous paper [3b] and the  $(\text{H}_0)_{\text{I}}$  and  $\delta_{\text{H}}$  values of this investigation, one gets the relations given in Fig. 6 and 7. Both parameters for acidities yield good correlations with  $\log k_{\text{ex}}$ ; for  $(\text{H}_0)_{\text{I}}$  one obtains a slope (a) of  $-0.902$  with a correlation coefficient (r) of 0.995 (Fig. 6). In the previous paper the respective values based on  $(\text{H}_0)_{\text{I}}$  determinations in absence of formaldehyde were  $a = -0.634$ ,  $r = 0.998$ .

Taking the chemical shift  $\delta_{\text{H}}$  as the acidity parameter (Fig. 7), the slope is  $a = -0.703$  with  $r = 0.998$ . In these purely aqueous system therefore  $(\text{H}_0)_{\text{I}}$  and  $\delta_{\text{H}}$  are equally well suitable for a quantitative description of the acid catalysis in cellulose formal formation<sup>6)</sup>.

The situation is, however, completely different for the rates of cellulose formal formation in water/acetic acid systems containing 17.5% HCl. In the previous paper [3a] we reported that there is no interpretable correlation between  $(\text{H}_0)_{\text{I}}$  (measured without formaldehyde) and  $\log k_{\text{ex}}$ . For comparative purposes with the following results we calculated the respective slope ( $a = -0.095$ ) and the correlation coefficient

<sup>6)</sup> Another problem is the mechanistic interpretation of these and other acid catalyzed reactions in moderately or strongly acidic solutions. See *e.g.* [3] [5d] and papers by *Bunnell et al.* [13].

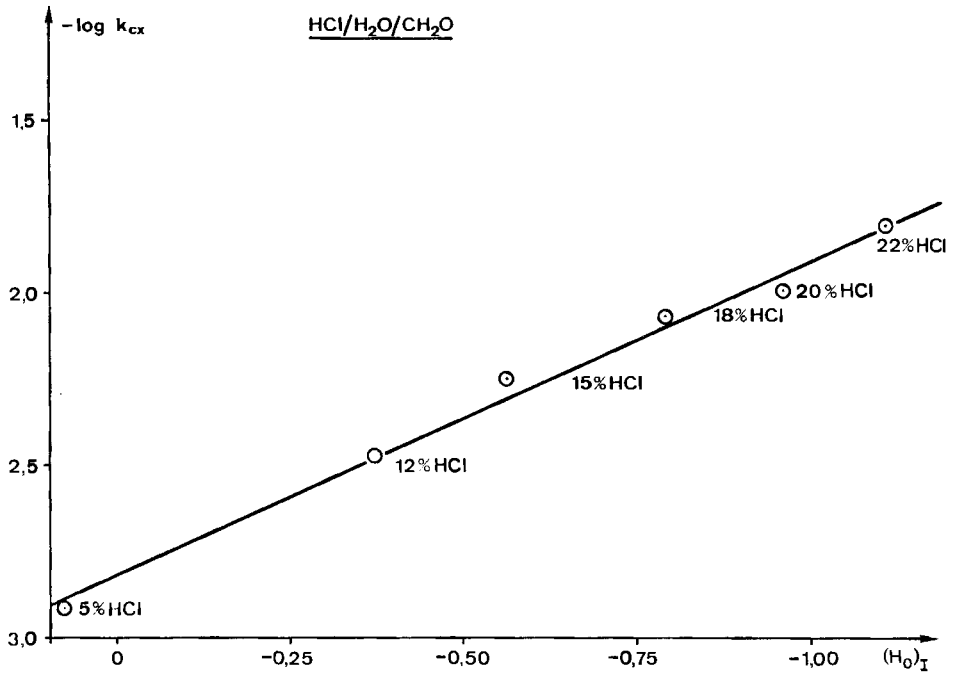


Fig. 6. Rate of cellulose formal formation in aqueous HCl versus the acidity function  $(H_0)_I$

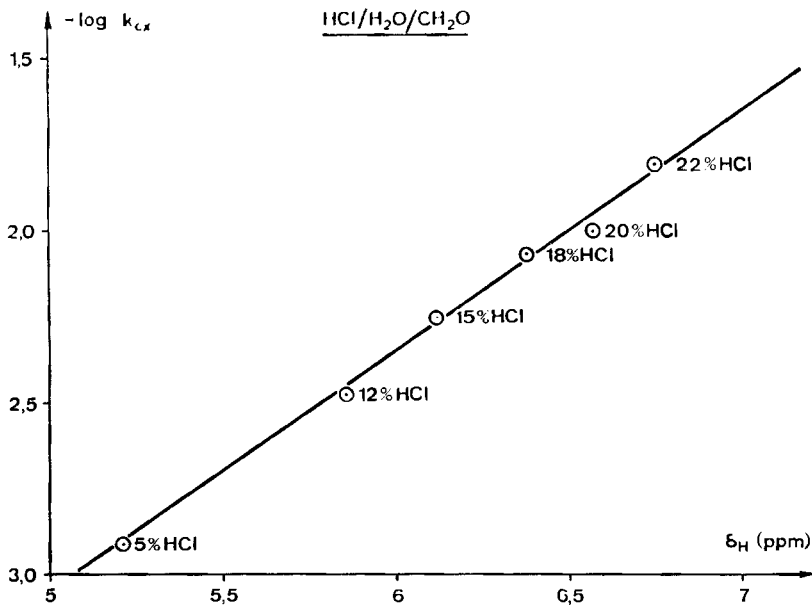


Fig. 7. Rate of cellulose formal formation in aqueous HCl versus chemical shift  $\delta_H$

( $r = 0.1425$ ) for the value in the previous paper<sup>7)</sup>). However, taking the  $(H_o)_I$  values determined in presence of formaldehyde a good correlation is obtained ( $a = -4.38$ ,  $r = 0.977$ ). This is particularly remarkable as the rate is not a steady function of the water/acetic acid ratio, but goes through a rate maximum at an intermediate ratio of solvent composition. Although this maximum can hardly be rationalized mechanistically, it parallels the change in  $(H_o)_I$ . Fig. 8 shows this relation between  $(H_o)_I$  and  $\log k_{cx}$ .

In contrast to that good correlation, the chemical shift is not a suitable parameter for the investigation of acid catalyzed reactions in the system  $HCl/H_2O/HOAc/CH_2O$  ( $a = -0.112$ ;  $r = 0.335$ )<sup>8)</sup>.

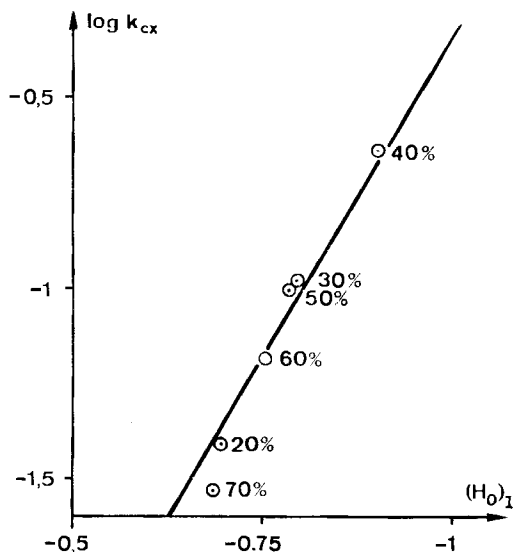


Fig. 8. Rate of cellulose formal formation in 17.5%  $HCl/H_2O/HOAc$  mixtures (Figures refer to the water content of the system)

In the previous communication [3] we reported also on the rate of depolymerisation (hydrolysis) of cellulose in aqueous hydrochloric acid solutions containing formaldehyde, based on  $(H_o)_I$  measurements in formaldehyde-free solutions. A logarithmic plot of the rate constant  $k_{hy}$  versus  $(H_o)_I$  (without formaldehyde) yielded a linear relationship ( $r = 0.936$ ). The slope ( $a = 0.219$ ) was significantly smaller than in the respective systems not containing formaldehyde, where a slope  $a = 0.288$  ( $r = 0.938$ ) was found.

Using our experimentally determined  $(H_o)_I$  values for systems containing formaldehyde,  $\log k_{hy}$  correlates for aqueous hydrochloric acid in presence of 7.5%  $CH_2O$  with  $(H_o)_I$  to give a slope of  $-0.323$  ( $r = 0.948$ ). Plotting  $\log k_{hy}$  versus  $\delta_H$  yields a slope of 0.246 with a correlation

- 7) Fig. 8 in our previous paper [3] was the basis for the calculation of the rate constants  $k_{cx}$ . The rate constant given there for the system containing 50% water ( $k_{cx} = 6.6 \times 10^{-2} s^{-1}$ ) was erroneously obtained from the later part of the reaction (straight line indicated with '50' in Fig. 5 of that paper). As discussed there, *initial* slopes should be taken. For the evaluation in the present paper we took therefore the appropriate value  $k_{cx} = 1.04 \times 10^{-1} s^{-1}$ .
- 8) We emphasize that this statement applies to that system only; definitely, it should not be generalized; yet, it should be kept in mind whenever chemical shifts are used as measures for acidities in complex systems.

coefficient of 0.928. In our opinion it cannot be decided if  $(H_0)_I$  or  $\delta_H$  is a more appropriate parameter for the rate of this reaction.

Based on the tentative explanations suggested above for the increasing influence of formaldehyde on the acidity in systems of small water content, we think that it might be feasible to assume that cationic proton donors other than  $H_3O^+$  may be effective for the acid catalyzed hydrolysis of cellulose. However, we have to emphasize again, that the intrinsic difficulties in the mechanistic analysis of reactions in moderately to strong acidic media do not allow any definitive conclusions at this time.

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## 78. Synthesis of 2,5-Diphenylbenzocyclopropene and 7,7-Dideuteriobenzocyclopropene<sup>1)</sup>

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*Summary.* Die Reduktion von 7,7-Dichloro-2,5-diphenylbenzocyclopropen<sup>1)</sup> (**1**) mit Aluminiumhydrid liefert in 50% Ausbeute 2,5-Diphenylbenzocyclopropen (**2**). Aluminiumdeuterid wandelt 7,7-Difluorobenzocyclopropen (**3**) in 7,7-Dideuteriobenzocyclopropen um.

In connection with mechanistic studies [1] [2] a sample of 7,7-dideuteriobenzocyclopropene<sup>1)</sup> was needed. Although the original benzocyclopropene synthesis of *Vogel* [4] offers a straightforward way to the deuterated compound, an alternative approach was sought which would allow introduction of the deuterium atoms in the very last step of the sequence. The readily accessible 7,7-dichloro-2,5-diphenyl-

<sup>1)</sup> The numbering used here and in the literature [3] for the benzocyclopropene skeleton does not agree with the IUPAC rules [1]. The correct numbering would be 1,1-dideuteriobenzocyclopropene and 1,1-dichloro-2,5-diphenylbenzocyclopropene for **1**, respectively.