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ACID–BASE STRENGTHS IN *m*-CRESOL

M. BOS AND E. A. M. F. DAHMEN
Department of Chemical Technology, Twente University of Technology, Enschede (The Netherlands)

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The strength of an acid in solution depends on properties of the solvent such as its dielectric constant and basicity. In order to study the relation between the acidity of a compound and the basicity of the solvent the simplest way is to compare the acid strengths of a compound in solvents with the same dielectric constants. The dielectric constants of *m*-cresol and pyridine are almost the same, *viz.* 12.29 and 12.3 respectively at 25°. Thus the difference in acid strengths of a compound in the two solvents should be explained by the fact that *m*-cresol has weakly protogenic properties whereas pyridine has weakly protophilic properties. The acid strength in pyridine of a number of compounds is already known[1,2]. From the determination of the acid strength in *m*-cresol for these compounds, the influence of the basicity of the solvent can be found.

If it is assumed that *m*-cresol shows self-dissociation

$$2\mathrm{HCres} \overset{K_s}{\rightleftharpoons} \mathrm{H_2Cres^+ + Cres^-} \qquad (1)$$

the dissociation equilibria for acids and bases in this solvent resemble those in acetic acid[3].

$$\mathrm{HX + HCres} \overset{K_i^{\mathrm{HX}}}{\rightleftharpoons} \mathrm{H_2Cres^+X^-} \overset{K_d^{\mathrm{H^+X^-}}}{\rightleftharpoons} \mathrm{H_2Cres^+ + X^-} \qquad (2)$$

$$\mathrm{B + HCres} \overset{K_i^{\mathrm{B}}}{\rightleftharpoons} \mathrm{BH^+Cres^-} \overset{K_d^{\mathrm{BH^+\,Cres^-}}}{\rightleftharpoons} \mathrm{BH^+ + Cres^-} \qquad (3)$$

For conductimetric and potentiometric studies the overall dissociation equilibria are more important

$$\mathrm{HX + HCres} \overset{K_{\mathrm{HX}}}{\rightleftharpoons} \mathrm{H_2Cres^+ + X^-} \qquad (4)$$

$$\mathrm{B + HCres} \overset{K_{\mathrm{B}}}{\rightleftharpoons} \mathrm{BH^+ + Cres^-} \qquad (5)$$

These overall dissociation constants, K_{HX} and K_{B}, were determined from conductimetric experiments and from potentiometric titrations.

EXPERIMENTAL

Chemicals

m-Cresol. This solvent (Merck, "Zur Synthese") was purified by keeping it in contact with activated molecular sieve 3A (Union Carbide) for 48 h, distillation at

200° under nitrogen and again drying over molecular sieve for 48 h. Solutions with this *m*-cresol were prepared under dried nitrogen. The water content of the solutions prepared in this way was below 0.01% (Karl Fischer titration).

Acids. Solutions of hydriodic, hydrobromic and hydrochloric acids were prepared by bubbling the dry gases (Baker) through *m*-cresol. Picric acid (Merck), 2,4-dinitrobenzenesulfonic acid (Eastman Kodak), benzenesulfonic acid (Riedel de Haan), benzoic acid (Merck), acetic acid (Merck), and iodoacetic acid (Merck) were used as received (reagent grade). 2,4,6-Trinitrobenzenesulfonic acid (K & K) was recrystallized from alcohol/ether before use.

Bases. Aniline (Merck, reagent grade), α-naphthylamine (Merck, reagent grade), strychnine (Merck, reagent grade), morpholine (Merck, reagent grade), butylamine (Fluka, reagent grade), triethylamine (Koch-Light, reagent grade), dimethylaminoazobenzene (Merck, indicator grade) and methyl orange (Merck, indicator grade) were used as received.

Salts. The salts of tetramethylguanidine (TMG) with various acids were prepared by neutralizing the tetramethylguanidine in ethanol with the acid and recrystallizing the product that was formed twice from ethanol/ether

In some cases the purity of the salt was checked by determination of the nitrogen-, sulfur- or chloride-content. The results are given below:

TMG–hydrochloric acid, m.p. 208° : %Cl 23.45 theor., 23.53 found ; %N 27.72 theor. 27.86 found.

TMG–benzenesulfonic acid, m.p. 145° · %S 11.61 theor., 11.80 found; %N 15.38 theor., 14.59 found.

TMG–picric acid, m.p 130° : %N 24.41 theor., 24.45 found.

Morpholine–2,4-dinitrobenzenesulfonic acid, m.p. 260° : %S 9.56 theor., 9.45 found %N 12.53 theor., 12.39 found.

TMG–hydrobromic acid, m.p. 188° ; TMG–2,4-dinitrobenzenesulfonic acid, m.p 145°.

Apparatus

In the conductimetric experiments a Radiometer conductivity cell type CDC 114 was used in combination with the Radiometer conductivity meter type CDM 2^{d} The conductivity measurements were carried out at 20±0.1°. The cell constant was determined to be 0.539 cm with freshly prepared potassium chloride solutions.

For the potentiometric titrations a Radiometer glass electrode, type G2222C was used. An Ag/AgCl electrode filled with a saturated solution of tetramethylammonium chloride in *m*-cresol was used as a reference electrode. When not in use the glass electrode was stored in an aqueous buffer pH 7. The potentiometric titration curves were recorded with a Radiometer titration assembly consisting of recorder SBRc, pH meter PHM26 and titrator TT111. Titration curves were reproducible within ±5 mV.

RESULTS

Conductivity measurements

The specific conductivities of acids, bases and salts were determined in *m*-cresol for dilution series of these compounds. From these measurements overal

TABLE I

CONDUCTIVITY MEASUREMENTS IN *m*-CRESOL[a]

2,4-Dinitrobenzenesulfonic acid		*Tetramethylguanidine*		*Hydrochloric acid*		*TMG-2,4-dinitrobenzenesulfonic acid*		*Morpholine*	
Conc 10^3	Λ	*Conc* 10^3	Λ	*Conc* 10^3	Λ	*Conc* 10^3	Λ	*Conc* 10^3	Λ
0.100	835	0.0916	4960	0.657	127	0.100	3060	1.38	87.1
0.200	788	0.183	4110	1.31	92	0.200	2740	2.76	63.9
0.300	772	0.274	3690	1.97	71	0.300	2440	4.13	51.5
0.400	742	0.366	3370	2.63	53	0.400	2200	5.51	45.4
0.500	724	0.458	3180	3.29	48	0.500	2060	6.89	41.9
0.700	649	0.549	3060	3.94	45	0.600	2020	8.27	37.1
1.00	603	0.732	2720	5.26	37	0.800	1770	11.0	34.5
2.00	468	0.916	2560	6.57	32	1.00	1640	13.8	33.0
3.00	411	1.83	1830	13.1	29	2.00	1300	27.6	21.9
4.00	369	2.74	1620	19.7	21	3.00	1150	41.3	18.2
5.00	343	3.66	1460	26.3	18	4.00	1030	55.1	15.6
6.00	323	4.58	1350	32.9	18	5.00	970	68.9	14.1
7.00	306	5.49	1250	39.4	16	6.00	924	82.7	13.0
10.0	280	9.16	1050	52.6	21	8.00	810	110	11.1
20.0	230	18.3	931	65.7	16	10.0	723	138	10.2
30.0	208	27.5	850						
40.0	197	36.6	851	Λ_0	3550[b]	Λ_0	4850	Λ_0	5800[b]
50.0	200	45.8	850						
60.0	191	54.9	816	K_{HX}	$3.8 \cdot 10^{-7}$	$K_{BH^+X^-}$	$1.0 \cdot 10^{-4}$	K_B	$2.8 \cdot 10^{-7}$
70.0	193	73.2	790						
80.0	187	91.6	753						
Λ_0	1460	Λ_0	9400						
K_{HX}	$1.3 \cdot 10^{-4}$	K_B	$5.7 \cdot 10^{-5}$						

[a] Concs in mol l^{-1}, Λ in ohm^{-1} cm^2 eq^{-1} 10^3

[b] Λ_0 calculated from eqn (6)

dissociation constants in m-cresol of the compounds were calculated by the Fuoss and Kraus method[4] In the calculations the value 12.5 for the dielectric constant[5] and the value 0.208 P for the viscosity[6] of m-cresol were used.

For various compounds the equivalent conductance became constant at higher concentrations. This can be explained by the formation of triple ions[7]. The formation constants of these triple ions were estimated for a number of acids by the method given by French and Roe[8]. In the calculations of the dissociation constants of benzenesulfonic acid and hydrochloric acid, it was necessary to calculate the equivalent conductivity of these compounds at zero concentration from the formula.

$$(\Lambda_0)_{HX} = (\Lambda_0)_{\substack{\text{2,4-dinitro-}\\ \text{benzene-}\\ \text{sulfonic}\\ \text{acid}}} - (\Lambda_0)_{\substack{\text{TMG-2,4-}\\ \text{dinitro-}\\ \text{benzene-}\\ \text{sulfonic}\\ \text{acid}}} + (\Lambda_0)_{TMGHX} \tag{6}$$

A typical part of the experimental and calculated data is given in Table I.

Table II gives the collected dissociation constants in m-cresol determined by conductivity measurements. The triple ion formation constants $K_{HX_2^-}$ are given in Table III for a number of acids.

TABLE II

DISSOCIATION CONSTANTS IN m-CRESOL DETERMINED CONDUCTIMETRICALLY

Compound	*Dissoc const*[a]	*Compound*	*Dissoc const.*
2,4-Dinitrobenzenesulfonic acid	$1.3 \cdot 10^{-4}$	n-Butylamine	$1.5 \cdot 10^{-5}$
Hydrobromic acid	$4.4 \cdot 10^{-5}$	Morpholine	$2.8 \cdot 10^{-7}$
Hydriodic acid	$4.1 \cdot 10^{-5}$	TMG–benz. sulf acid	$2.7 \cdot 10^{-5}$
Benzenesulfonic acid	$5.5 \cdot 10^{-7}$	TMG–2,4-dinitrobenz sulf acid	$1.0 \cdot 10^{-4}$
Hydrochloric acid	$3.8 \cdot 10^{-7}$	TMG–picric acid	$1.7 \cdot 10^{-4}$
2,4,6-Trinitrobenzenesulfonic acid	$2.6 \cdot 10^{-4}$	TMG–hydrochloric acid	$3.7 \cdot 10^{-5}$
Tetramethylguanidine	$5.7 \cdot 10^{-5}$	TMG–hydrobr acid	$3.7 \cdot 10^{-5}$
Triethylamine	$3.0 \cdot 10^{-5}$	Morpholine–2,4-dinitrobenz sulf acid	$8.6 \cdot 10^{-5}$

[a] In mol l^{-1}

TABLE III

TRIPLE ION FORMATION CONSTANTS $K_{HX_2^-}$ DETERMINED FROM CONDUCTIVITY MEASUREMENTS

Compound	$K_{HX_2^-}$
2,4-Dinitrobenzenesulfonic acid	$1 \cdot 10^3$
Hydrobromic acid	$5 \cdot 10^2$
Hydriodic acid	$3 \cdot 10^2$
2,4,6-Trinitrobenzenesulfonic acid	$3 \cdot 10^3$

[a] In $mol^{-1} \cdot l$

Potentiometric titrations

The curves of the potentiometric titrations of an acid HX with a base B in m

cresol could be explained, if it is assumed that besides acid-dissociation (eqn. 4), base-dissociation (eqn. 5) and self-dissociation (eqn. 1), the following equilibria also occur.

$$HX + X^- \overset{K_{HX_2^-}}{\rightleftharpoons} HX_2^- \tag{7}$$

$$BH^+ + X^- \overset{1/K_{BH^+X^-}}{\rightleftharpoons} BH^+X^- \tag{8}$$

The assumption of the formation of HX_2^-, necessary for the explanation of the titration curves, is in agreement with the conductimetric results.

Calibration of the glass electrode. The curve for the titration of hydrobromic acid with tetramethylguanidine in *m*-cresol was calculated up to about the equivalence point by the method described earlier[1] In this calculation the values of K_{HX}, $K_{HX_2^-}$, K_B and $K_{BH^+X^-}$ determined from the conductivity measurements were used.

From the formula

$$E_{mV} = E_0 - 59 \text{ pH} \tag{9}$$

with

$$\text{pH} = -\log a_{(H_2Cres^+)} \tag{10}$$

for the behaviour of the glass electrode, the value of E_0 was determined from the calculated and experimental curve of this titration. The results are given in Table IV.

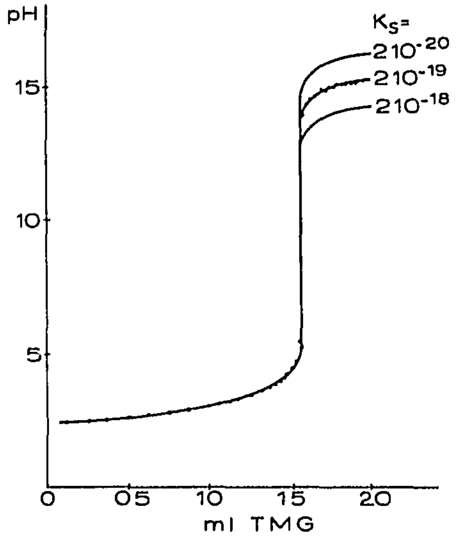
Determination of the self-dissociation constant of m-*cresol.* The self-dissociation constant of *m*-cresol, K_s, was determined from the part after the equivalence point of

TABLE IV

CALIBRATION OF THE GLASS ELECTRODE WITH THE TITRATION OF 4.00 ml OF 0.0391 *N* HYDROBROMIC ACID WITH 0.1004 *N* TETRAMETHYLGUANIDINE

ml TMG	*pH calculated*	*mV*	E_0 *calculated (mV)*
0.125	2.40	846	987
0.250	2.57	831	973
0.375	2.59	826	976
0.500	2.63	821	976
0.625	2.72	811	972
0.750	2.82	801	967
0.875	2.94	796	970
1.000	3.08	776	959
1.050	3.14	771	956
1.125	3.25	771	964
1.175	3.33	766	963
1.250	3.47	756	961
1.325	3.65	746	961
1.375	3.80	741	965
1.400	3.88	731	960
1.425	3.98	726	961
1.450	4.10	721	963
1.475	4.25	716	967
1.500	4.44	701	963
	Mean value of E_0		966

the curve of the titration of hydrobromic acid with tetramethylguanidine. Then the titration curve was calculated with various values of K_s (Fig. 1). The value $2{\cdot}10^{-19}$ gave the best fit between calculated and experimental titration curve



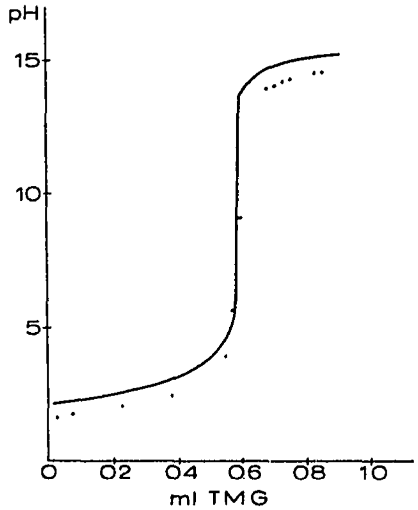
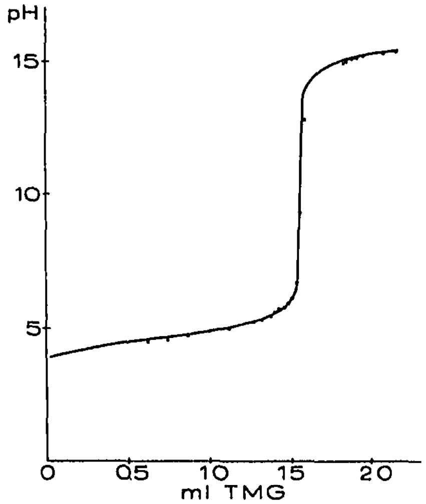


Fig 1. Titration of 4 00 ml of 0 0391 *N* hydrobromic acid with 0 1004 *N* tetramethylguanidine in *m*-cresol (.. .) Experimental curve; (——) calculated curve

Fig 2 Titration of 3 00 ml of 0.0213 *N* hydriodic acid with 0 1072 *N* tetramethylguanidine (.. .) Experimental curve, (——) calculated curve



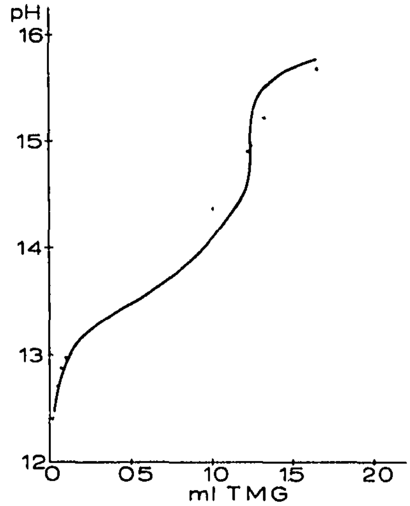


Fig 3 Titration of 4 00 ml of 0 0250 *N* benzenesulfonic acid with 0 0645 *N* tetramethylguanidine (...) Experimental curve, (——) calculated curve

Fig 4. Titration of 2.0 ml of 0 0720 *N* benzoic acid with 0 1164 *N* tetramethylguanidine (..) Experimental curve; (——) calculated curve

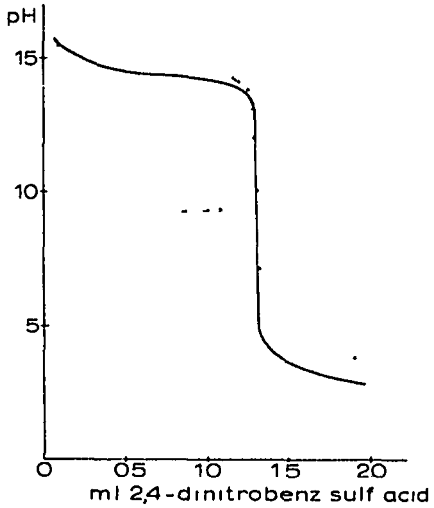
TABLE V

ACID-DISSOCIATION CONSTANTS AND TRIPLE ION FORMATION CONSTANTS FROM POTENTIOMETRIC TITRATIONS

Compound	K_{HX} (*mol l*$^{-1}$)	$K_{HX_2^-}$ (*l·mol*$^{-1}$)
2,4,6-Trinitrobenzenesulfonic acid	10^{-5}	10^{3}
2,4-Dinitrobenzenesulfonic acid	10^{-4}	10^{3}
Hydriodic acid	10^{-4}	10^{4}
Benzenesulfonic acid	10^{-6}	10^{2}
Hydrochloric acid	10^{-6}	10^{3}
Picric acid	10^{-12}	10^{2}
Iodoacetic acid	10^{-13}	—
Benzoic acid	10^{-15}	—
Acetic acid	10^{-16}	—

Potentiometric determination of dissociation constants of acids and bases The curves of the potentiometric titrations of various acids with tetramethylguanidine were determined with a calibrated glass electrode. From these curves the dissociation constants of the acids (K_{HX}) and the formation constants of HX_2^- ($K_{HX_2^-}$) were found in the following way. The known values of K_B, K_s, $K_{BH^+X^-}$ and estimated values of K_{HX} and $K_{HX_2^-}$ were applied in equilibria (1), (4), (5), (7) and (8), in order to calculate the titration curves. In the cases where $K_{BH^+X^-}$ was not known from conductivity measurements, a value of 10^{-4} was used. The estimated values of K_{HX} and $K_{HX_2^-}$ were changed by one p*K*-unit at a time until the best fit between calculated and experimental titration curve occurred. Some typical examples of the titration curves are given in Figs. 2, 3 and 4. The results are summarized in Table V.

The dissociation constants of several bases were determined from the curves of the titrations of the bases with 2,4-dinitrobenzenesulfonic acid. Here the curves



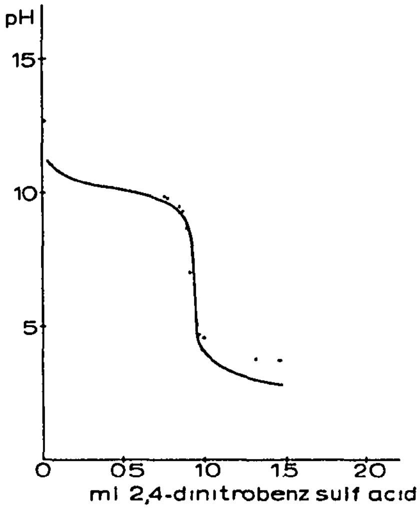


Fig 5 Titration of 3.0 ml of 0.0439 *N* *n*-butylamine with 0.100 *N* 2,4-dinitrobenzenesulfonic acid (. . .) Experimental curve, (———) calculated curve

Fig 6. Titration of 2 ml of 0.04588 *N* aniline with 0.100 *N* 2,4-dinitrobenzenesulfonic acid. (. ..) Experimental curve; (———) calculated curve were also calculated with the equilibria (1), (4), (5), (7) and (8). In the calculations, an estimated value of K_B was used, while for the other equilibrium constants the earlier determined values were used. Some typical titration curves of bases are represented in Figs. 5 and 6. The results are given in Table VI.

TABLE VI

BASE-DISSOCIATION CONSTANTS FROM POTENTIOMETRIC TITRATIONS

Compound	K_B
Triethylamine	$7\ 10^{-5}$
n-Butylamine	$2\ 10^{-5}$
Morpholine	$2\ 10^{-6}$
Strychnine	$2\ 10^{-6}$
Aniline	$2\ 10^{-10}$
α-Naphthylamine	$2 \cdot 10^{-10}$
Methyl orange	$2\ 10^{-8}$
Dimethylaminoazobenzene	$2\ 10^{-8}$

DISCUSSION

In the conductivity measurements as well as the potentiometric titrations, it is necessary to assume the formation of the complex HX_2^- to explain the experimental results. It is improbable that in *m*-cresol HX_2^- is a homoconjugate because this medium is a good hydrogen bond donor[9]. A triple ion of the form $X^-H^+X^-$ is more probable. The fact that the formation constant $K_{HX_2^-}$ of these complexes is large for those compounds which are completely ionized in *m*-cresol (determined spectrophotometrically for 2,4-dinitrobenzenesulfonic acid) is in agreement with this.

In cases in which dissociation constants were determined from potentiometric titrations as well as from conductivity measurements, the results are in agreement with each other (Table VII)

As pyridine and *m*-cresol have almost equal dielectric constants, the difference between the pK_a value in *m*-cresol and the pK_a value in pyridine for different acids

TABLE VII

COMPARISON OF p*K* VALUES FROM CONDUCTIVITY MEASUREMENTS AND POTENTIOMETRIC TITRATIONS

Compound	pK_{HX}/pK_B*titr*	pK_{HX}/pK_B*cond*	$K_{HX_2^-}$*titr*	$K_{HX_2^-}$ *cond*
2,4,6-Trinitrobenzenesulfonic acid	5	3 6	10^3	$3\ 10^3$
2,4-Dinitrobenzenesulfonic acid	4	3 9	10^3	$1\ 10^3$
Hydriodic acid	4	4 4	10^4	$3\ 10^2$
Hydrobromic acid	4 4	4 4	$5\ 10^2$	$5\ 10^2$
Benzenesulfonic acid	6	6 3	10^2	
Hydrochloric acid	6	6 4	10^3	
Morpholine	5 7	6 6		
n-Butylamine	4 7	4 8		
Triethylamine	4 2	4 5		

TABLE VIII

COMPARISON OF pK_a VALUES IN *m*-CRESOL, PYRIDINE AND WATER

Compound	pK_a (*cresol*)	pK_a (*pyr*)	pK_a (H_2O)	pK_a (*cresol*) $-$ pK_a (*pyr*)
2,4,6-Trinitrobenzenesulfonic acid	3.6^a		—	
2,4-Dinitrobenzenesulfonic acid	3.9^a		—	
Hydriodic acid	4.4^a	3.4^b	—	1.0
Hydrobromic acid	4.4^a	4.4^b	—	0.0
Benzenesulfonic acid	6.3^a		—	
Hydrochloric acid	6.4^a	5.7^b	—	0.7
Picric acid	12^c	3.0	0.4	9.0
Iodoacetic acid	13^c		3.1	
Benzoic acid	15^c	11	4.2	4
Acetic acid	16^c	12	4.8	4
Dimethylaminoazobenzene H^+	11^c		3.5	
Methyl orange H^+	11^c		3.8	
α-Naphthylamine H^+	9^c		3.9	
Aniline H^+	9^c		4.6	
Strychnine H^+	13^c		8.0	
Morpholine H^+	12.1^a	3.5	9.6	8.6
n-Butylamine H^+	13.9^a	5.5	10.6	8.4
Triethylamine H^+	14.2^a	3.8	10.8	10.4
TMG H^+	14.5^a	9.6	12.3	4.9

[a] From conductivity

[b] Reference 10

[c] From titrimetric experiment

should be independent of charge type of the acid. For the ammonium-type acids and picric acid, this turned out to be so (Table VIII).

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SUMMARY

For various acids and bases dissociation constants were determined conductimetrically in *m*-cresol. A glass electrode was calibrated by means of some compounds with dissociation constants known from conductivity measurements. Potentiometric titrations with this calibrated glass electrode gave dissociation constants of some other acids and bases in *m*-cresol. The value $2 \cdot 10^{-19}$ was found for the self-dissociation constant of *m*-cresol. From the difference pK_a (cresol) − pK_a (pyridine) for those compounds having acid or base strengths which are not levelled either in pyridine or *m*-cresol, it was found that the solvent *m*-cresol has a basicity about 8 pK units less than that of pyridine.

RÉSUMÉ

On a déterminé les constantes de dissociation de divers acides et bases par conductométrie dans le *m*-crésol. Au moyen de quelques composés ayant une constante de dissociation mesurée par voie conductométrique une électrode de verre a été calibrée. Des titrages potentiométriques à l'aide de cette électrode ont donné les constantes de dissociation d'autres acides et bases en *m*-crésol. Ainsi on a obtenu une valeur de $2 \cdot 10^{-19}$ pour l'autodissociation du *m*-crésol. En partant de la différence pK_a(crésol) $- pK_a$(pyridine) pour les composés ayant des acidités ou basicités qui ne sont nivellées ni en pyridine, ni en *m*-crésol, on a trouvé que la basicité du *m*-crésol est d'environ 8 unités de pK inférieure à celle de la pyridine.

ZUSAMMENFASSUNG

Die Dissoziationskonstanten verschiedener Säuren und Basen in *m*-Kresol wurden konduktometrisch bestimmt. Mit Hilfe einiger Verbindungen, deren Dissoziationskonstanten aus Leitfähigkeitsmessungen bekannt sind, wurde eine Glaselektrode geeicht. Potentiometrische Titrationen mit dieser geeichten Glaselektrode ergaben Dissoziationskonstanten einiger anderer Säuren und Basen in *m*-Kresol. Für die Eigendissoziationskonstante von *m*-Kresol wurde der Wert $2 \cdot 10^{-19}$ gefunden. Aus der Differenz pK_a (Kresol) $- pK_a$ (Pyridin) jener Verbindungen, deren Säure- oder Basestärken noch in Pyridin noch in *m*-Kresol nivelliert wurden, ergab sich, dass die Basizität des Lösungsmittels *m*-Kresol etwa 8 pK-Einheiten geringer als die von Pyridin ist.

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