zinc, quadrivalent vanadium, titanium and sulfur is to be obtained. Large amounts of pentavalent vanadium are extracted; phosphoric acid and molybdenum pass into the ether layer with ferric iron.

Experiments are in progress to determine the formula of the iron compound in the ether phase, and to study the factors affecting the distribution between phases and the formation of two ether phases under certain conditions. Experiments are planned to determine the efficiency of isopropyl ether in the separation of other elements, such as gallium and thallium.

Summary

It has been shown that isopropyl ether offers marked advantages over ethyl ether for the extraction of ferric iron from aqueous hydrochloric acid solutions, giving a more efficient extraction over a wider range of acid concentrations than does ethyl ether. Data are given which show the effect of varying the hydrochloric acid concentration, the amount of ferric iron, the effect of the presence of alcohol and peroxide and the behavior of other elements commonly occurring with or alloyed with iron.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY INSTITUTE OF THE UNIVERSITY OF COPENHAGEN]

The Strength of Acids in Formamide

BY FRANK H. VERHOEK

As a part of the study of the behavior of acids and bases in various solvents being carried on in this Institute, it was undertaken to investigate the strengths of acids in formamide. This substance is particularly interesting in that it is reported by Walden[1] to have a dielectric constant greater than that of water. It is a colorless, odorless, hygroscopic liquid, denser and more viscous than water, freezing at +2.55°, and it is a good solvent for both inorganic and organic salts. The study is concerned with the determination of the strength constants of representative groups of acids in formamide, from measurements of the conductivity of acid–base mixtures in that solvent, and from measurements of the potential differences set up between a standard buffer solution and buffer solutions made up with the different acids.

Purification of the Solvent.—Formamide obtained commercially is frequently acid and contains ammonium formate. The latter is volatile enough so that it is not readily removed by distillation at reduced pressure; further, it is so largely solvolyzed that the ammonia is pumped off in the distillation, leaving formic acid, which then appears in the acid distillate. Any water present in the solvent during the distillation reacts with the formamide to form ammonium formate. Formamide reacts with strong bases and with phosphorus pentoxide. The method adopted finally for the purification was to add solid brom thymol blue directly to the formamide, and neutralize with sodium hydroxide, avoiding an excess. The neutral liquid is heated at 80–90° under an oil pump vacuum until distillation is about to begin, ammonia and some of the water formed by the neutralization being pumped off. During this time the formamide has turned acid again, by loss of ammonia both from the ammonium formate originally present and from that formed by reaction with the water from the neutralization. The neutralization with sodium hydroxide is repeated, and the liquid heated in a vacuum to incipient distillation. This time less water is formed by the neutralization, and consequently less acid from the reaction *water* → *ammonium formate* → *formic acid*. With a repetition of the process four or five times, even quite impure samples will remain neutral when distillation begins. The whole of the formamide is now distilled from the sodium formate by evaporation from the surface at 80–90° in a vacuum, neutralized again with sodium hydroxide and redistilled in the same fashion, collecting the last four-fifths. This material is neutral, melts at about 2.2°, and has a specific conductance of about 5×10^{-5}. The neutral distillate is now further purified by fractional crystallization in a water- and carbon dioxide-free atmosphere. From 400–500 cc. five or six fractions are removed, giving a final 100 cc. with a specific conductance of 1 or 2×10^{-6}. The fractions removed, together with the first portion from the distillation, are returned again for treatment with sodium hydroxide, distillation, and recrystallization.

Residues were recovered by the same method as that for the purification of the original substance.

The pure material is not stable; the conductance increases by a factor of eight or ten in ten days or two weeks. It was found, however, that if a stream of air, purified by passing through a train containing soda lime, calcium chloride, phosphorus pentoxide and cotton, was bubbled rapidly through the liquid, the conductance would remain low for a longer period. With certain samples a decrease of conductance occurred at first on bubbling air through the formamide, followed by an increase. The solvent was considered still sufficiently pure for use when the specific conductance was less than 3.5×10^{-6}; the large majority of the experiments, however, were made on material having

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[1] Walden, *Z. physik. Chem.*, **46**, 175 (1903).

a conductance between 1.0×10^{-6} and 2.0×10^{-6}. The lowest value found for the conductance in the course of the work was 6.2×10^{-7}; already the next day, however, the conductance of this sample had risen to 1.17×10^{-6}. The best previously reported value[2] is 1.58×10^{-6}. Data reported below indicate that the specific conductance of pure formamide is in the neighborhood of 10^{-10}.

The hygroscopic nature of formamide was tested by exposing 5.6 g. in a small beaker to the room atmosphere, the liquid having a free surface of about 9 sq. cm. There was a gain in weight of 0.2% in one hour, 1% in five and one-half hours, and 10% in one hundred and forty-one hours. It was found, however, that amounts of water even up to 1% had no large effect in either the conductance or potentiometric experiments, so no special precautions, beyond a reasonable care in preventing unnecessary exposure to air on transferring and pipetting, were taken to prevent contamination with moisture.

Conductance Experiments.—By measuring the conductivity of a solution containing an acid and a base, and knowing the equivalent conductance at various concentrations of the salt formed by the reaction between the acid and the base, the amount of salt present in the acid–base mixture can be calculated. Using the same base and several different acids, the amount of salt formed with the several acids will depend upon the strengths of the acids, so that the relative strengths of the acids with respect to that base may be obtained. With the help of suitable transition systems the strengths of another group of acids with respect to another base may be referred back to the first group and a continuous scale of acid strengths set up over the whole range. If the solvent is itself basic or acidic, a detectable part of the conductivity of the acid–base mixture may be due to the free acid or base still present, so that the measured value must be corrected for this in order to get the true value for the salt.

In the case of formamide the bases used were the solvent itself, pyridine, and α-picoline, covering a range of acids from the strongest down to *p*-nitrophenol. To study still weaker acids, stronger bases would be required; piperidine and benzylamine, however, were found to react with formamide, forming ammonia and a substituted formamide, while the strong tertiary amines, which would not be expected to react, were too insoluble, except for triethylamine, which volatilized so rapidly from the solution that the data were not reliable. The equivalent conductances in formamide of the salts formed by the acid–base reaction are not known; since the formamide could not be obtained in a really pure state, these values could not be obtained accurately. Extrapolation to infinite dilution of the equivalent conductances of potassium dichloroacetate, potassium benzenesulfonate and potassium picrate solutions, using the Onsager equation with an assumed dielectric constant of 90 and making no corrections for the self-conductance of the solvent, gave the values 22.1, 20.7 and 19.8. Davis, Putnam and Jones[3] report for the equivalent conductance at infinite dilution for tetramethylammonium iodide 24.3, and for sodium iodide 24, the lowest concentration observed being only 0.1 *M* in the first case and 0.02 *M* in the second. The value 22 has then been chosen as reasonable for the equivalent conductance; it has been taken the same for all the salts, and it has been assumed to be unchanged with change in concentration. The protolysis constants are increased by a factor of two by changing the value of the equivalent conductance used in calculating them from 25 to 20; no accuracy greater than, say, 0.2 *pK* unit can therefore be claimed for the results.

Since formamide is itself both an acid and a base, an acid or a base alone dissolved in formamide gives an appreciable increase in conductivity, so that the measured conductance of the acid–base mixture is not that due to the presence of the salt alone. To get the true value the increase in the conductance of the solvent due to the addition of acid alone was added to the increase in conductance due to the addition of base alone, and the sum subtracted from the increase in conductance when both acid and base were present at the same concentrations as in the first two cases. From these values of the conductance at the various concentrations, and the assumed value for the equivalent conductance, the concentration of the ions may be obtained; subtraction of this value from the stoichiometric concentrations of the acid and base added gives the concentration of the free acid and base present, so that the protolysis constant for the reaction

$$A_1 + B_2 \longrightarrow A_2 + B_1$$
$$K_{A_1B_2} = \frac{[A_2][B_1]}{[A_1][B_2]}$$

may be calculated. If the extent of salt formation is large, as with strong acids, the value obtained in this manner is a first approximation, since in correcting for the conductance due to the addition of acid alone and base alone, values have been used corresponding to concentrations of acid and base higher than those actually present in the final solution. A second approximation using values for the acid and base concentrations found in the first approximation could be made, but the difference between the first and second approximations amounts at the most to 0.03 *pK* unit; the error introduced by virtue of the uncertainty in the value for the equivalent conductance is greater than this, and such a second approximation has been omitted. In general, equivalent amounts of acid and base were used; in representative cases, an excess of one of the components was introduced. The protolysis constants for those experiments containing an excess checked with those in which equivalent amounts were present. The detailed data for an experiment with benzoic acid and picoline are given in

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[2] G. F. Smith, *J. Chem. Soc.*, 3257 (1931).

[3] Davis, Putnam and Jones, *J. Franklin Inst.*, **180**, 567 (1915).

TABLE I

PROTOLYSIS CONSTANT OF BENZOIC ACID AND α-PICOLINE

Concn.	Sp. cond. $\times 10^6$ Salt	Acid	Base	Increase $\times 10^6$ Salt	Acid	Base	Corr. cond. of salt	Concn. of ions	$K \times 10^2$
0.0	1.82	1.88	1.90	0.00	0.00	0.00	0.00		
.001	5.55	1.94	2.03	3.73	.06	.13	3.54	0.000161	3.68
.002	9.36	2.08	2.10	7.54	.20	.20	7.14	.0003246	3.76
.005	21.10	2.50	2.25	19.28	.62	.35	18.31	.0008324	3.99
.01	40.57	3.09	2.44	38.75	1.21	.54	37.00	.001686	4.11
.02	78.8	4.07	2.66	77.0	2.19	.76	74.0	.003364	4.08
.05	189.5	6.54	3.61	187.7	4.66	1.71	181.3	.008242	3.90
.1	361.0	10.17	4.51	359.2	8.29	2.61	348.3	.01583	3.53

Table I. It is evident that a possible increase in the protolysis constant with increasing salt concentration is not greater than the experimental error.

For the strong acids, where formamide itself acts as the base, a conventional dissociation constant was calculated, using Ostwald's dilution law and the value 22 for the equivalent conductance. There was some indication, from a comparison of the equivalent conductance–concentration curves for the strong acids benzenesulfonic and picric with those for the corresponding potassium salts, that the equivalent conductance at infinite dilution of an acid is two units less than that of its potassium salt, but no account has been taken of this difference. Table II gives the data for *o*-nitrobenzoic acid dissolved in formamide. The constants at lower concentrations are inaccurate, since the solvent itself has such a high conductivity that it amounts to a large fraction of the total.

TABLE II

THE DISSOCIATION CONSTANT OF *o*-NITROBENZOIC ACID IN FORMAMIDE

Sp. cond. of solvent: 1.54×10^{-6}

Concn.	Equiv. cond.	100α	$K \times 10^5$
0.000831	5.59	25.22	7.07
.001689	3.84	17.45	6.23
.002602	3.08	14.00	5.93
.00539	2.13	9.69	5.60
.01147	1.47	6.66	5.45
.02349	1.04	4.71	5.46
.04899	.73	3.31	5.55
.0929	.54	2.45	5.72
.1030	.51	2.34	5.76

$pK_{0.05} = 4.26$

The conductivity experiments were carried out at 20° in a small narrow cell of 15-cc. capacity with platinized electrodes, and a constant of 0.3827. To 5 cc. of solvent was added from a weight buret a solution roughly 0.2 *M* in acid and base, giving concentrations in the cell from slightly less than 0.001 up to 0.1 *M*. In the particular case of trichlorophenol a saturated solution of the acid is only 0.06 *M*, putting an upper limit to the concentration at which the experiments could be carried out. The density of the final solution in the cell was measured at the end of the experiment, and the density assumed to vary linearly with the concentration in calculating the concentrations from the weight data. Values at round concentrations for correcting for the conductances of the free acid and base were obtained from these original data by straight line interpolation. The three experiments required for the determination of the protolysis constant of an acid–base pair, namely, an experiment with both acid and base, one with acid alone and one with base alone, were always made on the same day, so as to have the solvent as nearly identical for the three as possible.

The negative logarithms of the strength constants determined from the conductance measurements are given in the second, third and fourth columns in Table V. The values given are those for the arbitrarily chosen stoichiometric concentration of acid or of acid and base 0.05 *M*. Picric acid and trichloroacetic acid are so strongly dissociated in formamide that the values given for them are uncertain; benzenesulfonic acid appears to be dissociated completely at all concentrations up to 0.1 *M*. The values in the third column have been obtained from the protolysis constants of the acids reacting with pyridine by the relation

$$pK_{AM} = pK_{AP} - pK_{SP} + pK_{SM}$$

where pK_{AM} is the negative logarithm of the conventional dissociation constant given in that column, K_{AP} is the protolysis constant for acid A reacting with the base pyridine, K_{SP} is the constant for salicylic acid and pyridine, and K_{SM} is the constant for salicylic acid and the pure solvent. An extension of this equation through benzoic acid chosen as a standard connects the data for pyridine with that for α-picoline, and so back to the pure solvent.

Potentiometric Experiments.—The potentiometric experiments were carried out with hydrogen electrodes in each of two compartments connected through stopcocks to a narrow U-tube filled with saturated potassium chloride (0.88 *M*) as a bridge. The potential was found to depend in part upon the rate at which the hydrogen was bubbled through the solutions in the two compartments. If the rate of bubbling was the same in the two compartments, a value of the potential difference constant over several hours was obtained; if the rate at which the hydrogen passed through one solution was greater than that in the other the potential difference rose or fell at a constant rate, but would return to a value near to the original value when the rate of bubbling was made equal in the two compartments again. The experiments were made using the same constant and equal rate for all. The substitution of quinhydrone for the hydrogen electrode proved to be of no advantage, since quinhydrone gradually darkens on standing with formamide, and there is a slow change in the potential difference. It is possible, however, to extrapolate back to an initial value, and a dissociation constant determined with the quinhydrone electrode in a case where hydrogen would have been unsuitable is included in the data reported. Junction potentials were neglected in all cases.

The standard buffer was a solution 0.05 M in potassium chloride, 0.05 M in anhydrous potassium salicylate and 0.05 M in salicylic acid. The pH of the salicylic acid–salicylate buffer was determined by measuring against benzenesulfonic acid, assuming complete dissociation of the latter. With this strong acid there was a slow decrease in potential with time, and the value used in calculating the pH is that obtained by extrapolating to zero time. The average of three experiments for which the maximum difference was 0.071 unit gave 4.358 for the pH of the standard buffer. The standard salicylate solution was made up anew for each experiment at the same time as the test solution, so as to have the two solutions as nearly comparable as possible. The test buffers in the case of the carboxylic acids were 0.05 M in potassium chloride, and 0.05 M in the potassium salt of the particular acid; they were made 0.02, 0.05 and 0.1 M in the acid by adding weighed amounts of acid to 5 cc. of salt solutions in the apparatus. The hydrogen ion concentrations in the test solutions were calculated from

$$\log [H^+] = E/0.05814 + \log [H^+]_{\text{salicylic–salicylate}}$$

where $\log [H^+]_{\text{salicylic–salicylate}}$ is -4.358. The pK for the acid is then found from

$$pK = -\log K = -\log [H^+] - \log [\text{base}] + \log [\text{acid}]$$

the stoichiometric concentrations of the acid and base present being corrected where necessary for the dissociation of the acid. The constants calculated for the three buffer ratios checked to about 0.1 logarithmic unit, and duplicate experiments checked with the same accuracy. An experiment with salicylic and benzoic acid buffers in which the buffer ratio was changed by adding salt to a 0.05 M acid solution showed that the effect of changing ionic strength on the dissociation constant is not greater than the experimental error. Table III gives the results for measurements on salicylic acid–benzoic acid buffer pairs under various conditions.

For the anilinium acids, the test solutions were made 0.05 M in potassium chloride, and 0.1 M in the anilinium chloride or benzenesulfonate; to a known volume of this solution in the electrode compartment was added one, two, or three drops of piperidine from a weight pipet, forming free base by the reaction

$$RNH_3^+ + C_5H_{11}NH \longrightarrow C_5H_{11}NH_2^+ + RNH_2$$

This reaction is complete with the strong acids and piperidine, and the piperidinium ion plays no part in determining the hydrogen ion concentration of the solution in the presence of the strong acids. Addition of piperidine in excess of 0.1 M gave a buffer solution in piperidine–piperidinium ion, from which the acid strength of piperidinium ion could be obtained. For benzylamine, triethylamine, and pyridine, the pure bases were added from a weight buret to solutions 0.05 M in potassium chloride and 0.05 M in the amine salt. With the amine bases present there is a change in potential difference with time due to the reaction with formamide. This change is not great; even with the strongest base piperidine it amounts only to one and one-half or two millivolts an hour, so that an extrapolation to the initial time is carried out easily. Readings were taken at fifteen-minute intervals until the rate of change remained constant for an hour, and the value obtained by extrapolating to zero time used in the calculations. About one-half hour was usually required for the system to come to equilibrium. With triethylamine, the triethylamine was bubbled out by the hydrogen so rapidly that the potential difference decreased by 10 mv. an hour. The correctness of the value reported for this substance, however, is indicated by the fact that the addition of further triethylamine to the solution, and extrapolation back to the moment of addition, gave values for the dissociation

TABLE III

DISSOCIATION CONSTANT OF BENZOIC ACID

Salicylic acid, m./l.	Potassium salicylate, m./l.	Benzoic acid, m./l.	Potassium benzoate, m./l.	E. m. f., mv.	$pK_{\text{benzoic acid}}$
0.05	0.05	0.02	0.05	131.4	6.220
		.05		108.8	6.229
		.1		90.6	6.217
.05	.05	.02	.05	135.6	6.292
		.05		112.1	6.286
		.1		92.4	6.248
.02	.05	.05	.05	88.8	6.283
.05				112.6	6.294
.1				130.8	6.307
.05	.02	.05	.05	133.7	6.260
	.05			111.9	6.282
	.1			96.7	6.288

TABLE IV

DISSOCIATION CONSTANT OF *o*-CHLOROANILINIUM ION

Time, min.	0.04371 M piperidine E. m. f., mv.	0.07638 M piperidine E. m. f., mv.
10		125.1
15	151.4	124.7
20	150.8	
30	150.4	124.8
45	150.6	124.6
60	150.5	124.4
75	150.4	124.2
90	150.2	124.0
105	150.1	123.8
120	149.9	
E. m. f. at zero time	151.0	125.2
pK	1.566	1.527

constant of the triethylammonium ion which agreed with the first, when the concentration of triethylamine added the first time was corrected for the amount which had bubbled away. Table IV gives the data for an experiment in which the dissociation of *o*-chloroanilinium ion was studied. To a solution 0.1 *M* in *o*-chloroanilinium chloride was added in the first half of the experiment piperidine corresponding to 0.04371 *M* per liter; to this solution was later added piperidine corresponding to 0.03267 *M* per liter. No correction was applied for the reaction of the amine with the formamide during the first half of the experiment in calculating the concentrations in the second half.

The *pK* values from the electrometric measurements are included in Table V. The values given for the carboxylic acids in the table are those for buffer solutions containing equal quantities of acid and salt; for the cation acids the values are those obtained from the first addition of piperidine or other amine.

TABLE V

THE DISSOCIATION CONSTANTS OF ACIDS IN FORMAMIDE

Acid	*pK* in H_2O	*pK* in formamide Solvent	Pyridine	Picoline	Potentiometric
Picric acid	0.3[a]	(1.20)			
Trichloroacetic acid	0.7[a]	1.46			
Dichloroacetic acid	1.3	2.85			2.60
2,4-Dichloroanilinium ion	2.14				1.08
α,β-Dibromopropionic acid	2.17	4.08			
o-Nitrobenzoic acid	2.19	4.28			
o-Chloroanilinium ion	2.68				1.57
Monochloroacetic acid	2.86	4.56	4.50		4.74
Salicylic acid	2.98	4.46	4.46[e]		4.36
m-Nitrobenzoic acid	3.45		5.30	5.41	
m-Chloroanilinium ion	3.54				2.75
2,6-Dinitrophenol	3.58	4.17			
m-Chlorobenzoic acid	3.81		5.75	5.72	5.70
2,4-Dinitrophenol	4.02	4.50	4.54		
p-Chloroanilinium ion	4.03				3.26
Benzoic acid	4.19		6.21	6.21[f]	6.27
Succinic acid I	4.20[h]				5.90
Anilinium ion	4.69				4.10
Propionic acid	4.87		7.02	6.98	7.18
Trimethylacetic acid	5.01		7.39	7.33	7.43
2,5-Dinitrophenol	5.12		6.00	5.94	
Pyridinium ion	5.26[b]				4.48
Succinic acid II	5.57[h]				7.89
2,4,6-Trichlorophenol	6.41		7.28	7.28	
p-Nitrophenol	7.15			8.53	8.51[g]
Benzylammonium ion	9.37[c]				9.77
Triethylammonium ion	10.97[d]				9.99
Piperidinium ion	11.13[b]				11.08

[a] Hall, *Chem. Rev.*, **8**, 191 (1931). [b] Hall and Sprinkle, THIS JOURNAL, **54**, 3478 (1932). [c] Carothers, Bickford and Hurwitz, *ibid.*, **49**, 2408 (1927). [d] Åkerlöf, *ibid.*, **50**, 739 (1929). [e] Standard value for transposing from base pyridine to base formamide. [f] Standard value for transposing from base picoline to base pyridine. [g] Measured with quinhydrone electrode. [h] Simms, *J. Phys. Chem.*, **32**, 1128 (1928).

The Ion Product of Formamide.—The ion product of the solvent, $K_M = [M^+] [M^-]$, was determined directly by measuring the potential difference between a solution of potassium hydroxide and the standard salicylate buffer, and combining these data with those for benzenesulfonic acid measured against the standard buffer. The reaction between potassium hydroxide and formamide does not have such a great effect on the potential difference as might be expected; the potential dropped at a steady rate of about 8 mv. an hour, and a value extrapolated back to the moment at which the solution was made was easily obtained. The potential difference between 0.0976 *M* KOH and the salicylate buffer was 669.7 mv.; between 0.0303 *M* KOH and the buffer 632.2 mv. For 0.02498 *M* benzenesulfonic acid against the buffer the potential difference was 157.6 mv.; for 0.06956 *M* benzenesulfonic acid 187.0 mv. These data make possible two independent calculations of the ion product. Even combining them to pairs in such a way that the difference between the two values of the ion product is greatest, the values obtained for pK_M

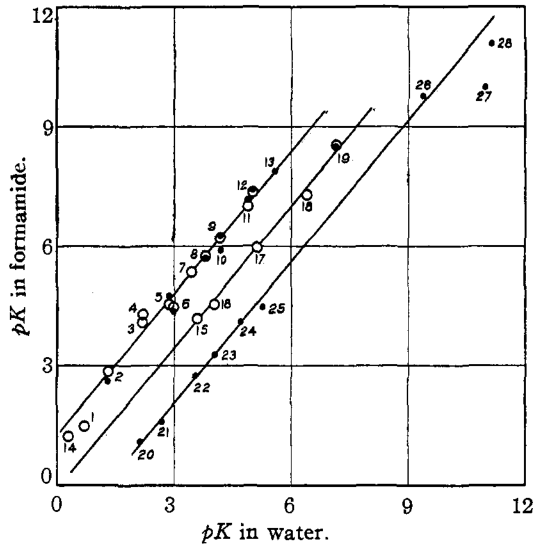

Fig. 1.—Logarithmic dissociation constants in formamide and water.

Circles, average of conductimetric values; dots, potentiometric values.

1, Trichloroacetic acid
2, Dichloroacetic acid
3, α,β-Dibromopropionic acid
4, *o*-Nitrobenzoic acid
5, Monochloroacetic acid
6, Salicylic acid
7, *m*-Nitrobenzoic acid
8, *m*-Chlorobenzoic acid
9, Benzoic acid
10, Succinic acid I
11, Propionic acid
12, Trimethylacetic acid
13, Succinic acid II
14, Picric acid
15, 2,6-Dinitrophenol
16, 2,4-Dinitrophenol
17, 2,5-Dinitrophenol
18, 2,4,6-Trichlorophenol
19, *p*-Nitrophenol
20, 2,4-Dichloroanilinium ion
21, o-Chloroanilinium ion
22, *m*-Chloroanilinium ion
23, *p*-Chloroanilinium ion
24, Anilinium ion
25, Pyridinium ion
26, Benzylammonium ion
27, Triethylammonium ion
28, Piperidinium ion

are: for 0.0303 M KOH and 0.02498 M $C_6H_5SO_3H$: 16.70; for 0.0976 M KOH and 0.06956 M $C_6H_5SO_3H$: 16.90. The agreement is good.

If $pK_M = 16.8$, and the equivalent conductance of a mixture of M^+ and M^- ions is 22, the value calculated for the specific conductance of the pure solvent is 9×10^{-11}.

Discussion

The data of Table V are plotted against the corresponding pK values for water in Fig. 1. Except as otherwise noted, the pK values for water for the carboxylic and cation acids are taken from the paper of Brønsted, Delbanco and Tovborg-Jensen;[4] the values for the phenols are from the Landolt–Börnstein "Tables." Some of the values for acids not included in the paper cited are for temperatures other than 20°. The slope of the curves as drawn is 1.19, *i. e.*, greater than unity. The slope usually found on plotting the logarithm of acid or basic dissociation constants in a non-aqueous solvent against the corresponding values in water is unity, and the latter slope is also predicted theoretically if the assumption is made that the effect of changing the medium is only to change the activity coefficients of the ions by virtue of the change in dielectric constant. It has been difficult to decide whether the unusual slope found in the formamide–water diagram is the result of experimental error. For the carboxylic acids, the only point which is greatly in doubt is that for trichloroacetic acid. The pK value for trichloroacetic acid in water is not too well known. The value given for formamide is probably too high rather than too low, since the change in the equivalent conductance with concentration has not been considered; consideration of this change would give the acid a larger dissociation constant. A determination of the potential difference between a trichloroacetic acid solution and the standard salicylate buffer using quinhydrone indicated that trichloroacetic acid is completely dissociated at 0.02 M, but as stated previously, the potential values with quinhydrone are not dependable. Consideration only of the pK values of the carboxylic acids obtained by potentiometric measurements would definitely give a curve with a slope greater than unity. For the phenols, the data are perhaps not numerous enough to serve as a basis for discussion; a curve drawn through the points with the same slope as for the other two acid types is at least not inconsistent with the positions of the points, with the exception of the point plotted for picric acid. A valid dissociation constant for picric acid cannot be calculated from conductivity data, since the degree of dissociation is too large. Direct comparison of the equivalent conductances at various concentrations of the three acids picric, trichloroacetic and benzenesulfonic given in Table VI shows picric acid to be much stronger than trichloroacetic acid, and nearly completely dissociated. In comparing the data it should be noted that the equivalent conductance at infinite dilution is evidently greater for trichloroacetic acid than for picric and benzenesulfonic acids. The value of pK actually calculated from the data for picric acid is given in Table V and plotted in the figure, but it is evident that it should be much less. In the curve for the cation acids, only the points for the primary amines can properly be compared, that is, the curve must be drawn through the points for the substituted anilines and benzylamine. One would of course expect a difference in slope if primary are compared with secondary or tertiary amines. A curve drawn through the points for the anilines and benzylamine must have a slope greater than unity.

TABLE VI

CONDUCTANCE OF STRONG ACIDS IN FORMAMIDE

Benzenesulfonic acid Sp. cond. of solvent 1.62×10^{-6}		Picric acid Sp. cond. of solvent 2.31×10^{-6}		Trichloroacetic acid Sp. cond. of solvent 2.87×10^{-6}	
Concn.	Equiv. cond.	Concn.	Equiv. cond.	Concn.	Equiv. cond.
0.000938	18.93	0.000789	18.58	0.000880	19.67
.001979	18.23	.001360	18.04	.001742	18.86
.002928	18.00	.002114	17.60	.002603	18.43
.006031	17.69	.004509	17.12	.005235	17.57
.01298	17.20	.009988	16.33	.01127	16.25
.02658	16.52	.02137	15.85	.02240	14.64
.05935	15.59	.04205	14.98	.04828	12.35
.1170	14.52	.09118	13.60	.1026	9.90

One is inclined to believe, then, that the anomalous slope of the curves is real. The curves have been drawn in such a way as to give all three the same slope; the possibility of some variation in slope in the three cases is not, however, excluded. The literature records another case in which the slope of a curve in a plot similar to that in Fig. 1 differs from unity, namely, the case of the singly charged cation acids in acetonitrile,[5] where the slope is only 0.47. The reason for this deviation is probably to be sought in a consti-

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[4] Brønsted, Delbanco and Tovborg-Jensen, *Z. physik. Chem.*, **A169**, 361 (1934).

[5] Kilpatrick and Kilpatrick, *Chem. Rev.*, **13**, 131 (1933).

tutional effect on the activity coefficients of the components of the solution. Such effects of structural differences in changing from one solvent to another are quite common, and must in any case be adduced to explain the difference between the carboxylic acids and the phenols. The unexpected in the case of formamide and acetonitrile is that such an effect should be operative over such a large range, and so consistently parallel to the acid strength. One usually finds a scattering of points on both sides of a line of the predicted unit slope, rather than a single line of a different slope. It is possible, of course, that the inclusion of more acids would give such a chance scattering about curves of unit slope.

The figure shows that if a carboxylic acid, a phenol, and a singly charged positive acid have the same strength in water, the phenol will be twenty-five times stronger than the carboxylic acid in formamide, and the cation acid five hundred times stronger. The difference between the carboxylic acids and the phenols must be due, according to the equation of Brønsted[6] $K_A = K_a f_A/f_B$ where K_a is a thermodynamic dissociation constant independent of the medium, K_A is the dissociation constant in the solvent concerned, and f_A and f_B are activity coefficients of the acid and the base in that solvent, to a change in the ratio of the activity coefficient of the acid to that of the base to a different extent for the two sorts of acids on passing from water to formamide. This change must be due to influences other than those of electric charge and dielectric constant, since, as far as the latter forces are concerned, the system is the same for carboxylic acids and phenols. An increase in the strength of certain phenols relative to carboxylic acids has been found for several other solvents—ethyl and methyl alcohols, *n*-butyl alcohol, acetonitrile—and has been attributed by Wynne-Jones[7] in the case of picric acid to the greater effective radius of the picrate ion compared to a carboxylate ion. The same treatment applied to the data in formamide, however, would require the phenolate ions to be smaller than the carboxylate ions.

In passing from an uncharged to a charged acid, the effect of the electric charge and dielectric constant should ordinarily become noticeable. In the particular case of a change from water to formamide, however, comparatively little effect resulting from the change in the dielectric constant should be observed. If the dielectric constant of formamide is taken as 100, the strength of a cation acid relative to an uncharged acid should be decreased by 0.125 logarithmic unit on passing from water to formamide, the calculation being made according to the equations developed by Brønsted,[6] using 5×10^{-8} cm. as the ionic radius. The actual difference found between the anilinium ions and the carboxylic acids is an increase of 2.7 units, which would correspond to a value of 15 for the dielectric constant of formamide. The dielectric constant of formamide has not been measured in this investigation, but it is hardly likely that it can be as low as this. Salts are, in general, easily soluble in formamide—simple salts such as potassium and sodium chloride are about one-fifth to one-sixth as soluble in formamide as in water, while the cobaltammines are either as soluble or often much more soluble in formamide than in water—which would indicate that it has a high dielectric constant. Experiments on the change of solubility with ionic strength of the 2–1 salts chloropentammine cobalt chloride, bromopentammine cobalt bromide and *trans*-dinitrotetrammine cobalt sulfate in solutions of potassium thiocyanate and sodium formate gave limiting slopes at infinite dilution of 0.7, 0.6 and 0.9. The results are obscured by the initial contamination of the solvent with salt, as observable in its high conductivity, but the slopes are in all three cases less than the value 1.0 calculated for a 2–1 salt in water, indicating that the dielectric constant is higher than that of water. At concentrations above 0.005 *M*, where the conductivity of the solvent is no longer such a disturbing factor, the change of conductance with concentration of the three salts potassium dichloroacetate, potassium benzenesulfonate and potassium picrate is in fair agreement with that to be expected from the Onsager equation, assuming the dielectric constant to be 90. From cryoscopic measurements Walden[8] concluded that potassium iodide, tetramethylammonium iodide, and other alkyl ammonium salts are as highly ionized in formamide as in water, indicating a high dielectric constant. The dielectric constant of formamide's nearest homolog, acetamide, is 60 in the liquid phase, and it is reasonable to expect that that of formamide should be at least as great. The increase in the strength of a cation

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[6] Brønsted, *Z. physik. Chem.*, **A169**, 52 (1934).

[7] Wynne-Jones, *Proc. Roy. Soc.* (London), **A140**, 440 (1933).

[8] Walden, *J. Chem. Soc.*, **102**, II, 26 (1912).

acid with respect to a carboxylic acid in passing from water to formamide must then be attributed to a more marked effect of the same influence which causes the increase in strength of a phenol as compared to a carboxylic acid, and to be not at all the result of a change in the dielectric constant. If the change in structure represented by a change from benzoic acid to 2,4-dinitrophenol, which have nearly the same strength in water, causes the strength to change by a factor of 25, it is evident that one cannot exclude the possibility of a further change by a factor of 20 on passing from 2,4-dinitrophenol to *p*-chloroanilinium ion.

Further light on this question would be given by a study of negatively charged acids such as acid salts of dicarboxylic acids. The theoretically predicted effect of the change in dielectric constant on the relative strengths of monocarboxylic acids and the acid salts of dicarboxylic acids is of the same (small) magnitude but opposite in sign to that predicted for a change to a cation acid. Further, one would not expect any enormous change in activity coefficient ratios in going from a mono- to a dicarboxylic acid, since these two are in any case more nearly similar than a carboxylic acid and a phenol or a carboxylic acid and an amine ion. The prediction would be, then, that a group of acids including both monocarboxylic acids and acid salts of dicarboxylic acids would show nearly the same relative strengths in formamide as in water. Unfortunately, of the normal salts of dibasic acids which were available—sodium and potassium oxalate, sodium tartrate, sodium malonate and sodium succinate—only the last named was sufficiently soluble for use in an acid salt–normal salt buffer, and the short time left did not permit the preparation of other salts. Values for the somewhat "overlapping" strength constants for succinic acid were calculated by the method of Simms[9] from the potential difference between sodium succinate–succinic acid mixtures and the standard buffer, and are given in Table V. On plotting the value for the second dissociation constant of succinic acid, the point is found to lie directly upon the curve for the other carboxylic acids, in agreement with the above prediction.

The observed difference between the carboxylic acids, the phenols and the cation acids in formamide shows that extreme care is necessary when attributing solely to a difference in charge type effects which may be due to the change in chemical type which is inextricably connected with the change in charge type.

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Summary

1. A simple method for the preparation of formamide having a specific conductance of 10^{-6} has been described. It consists in the distillation of formamide treated with sodium hydroxide, followed by a fractional crystallization.

2. From measurements of the conductivity of formamide solutions of free carboxylic acids and of mixtures of acids with pyridine and α-picoline, and the assumption of certain values for the equivalent conductances of the salts formed in the solutions, dissociation constants of the acids in formamide have been calculated.

3. Dissociation constants of a group of phenols in formamide have been obtained by the same procedure.

4. From measurements of the potential difference between buffer solutions of various carboxylic acids and a standard potassium salicylate–salicylic acid buffer, which was in turn compared with a benzenesulfonic acid solution, a scale of acid strengths in formamide independent of the conductivity measurements has been obtained. The dissociation constants obtained by the two methods are in agreement within the experimental error.

5. Dissociation constants of a group of singly charged cation acids have been obtained by the potentiometric method.

6. The value 10^{-17} has been found for the ion product of formamide by measurements of the potential difference between solutions of potassium hydroxide and benzenesulfonic acid and the standard buffer.

7. On plotting the negative logarithms of the dissociation constants of acids in formamide against the corresponding values in water, three straight lines of slope greater than unity, corresponding to the carboxylic acids, the phenols and the cation acids, have been obtained. The relative positions of the lines indicate that if a carboxylic acid, a phenol and a singly charged cation acid have the same strength in water, the phenol will be 25 times stronger than the carboxylic acid in formamide, and the cation acid 500 times stronger.

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[9] Simms, THIS JOURNAL, **48**, 1245 (1926).