tion wherein an insoluble solid is brought into solution with an attendant change in hydrogen ion concentration. Naturally the use of substances which react with the quinhydrone electrode, as employed in these measurements, is excluded.

Summary

1. Experimental evidence is presented leading definitely to the conclusion that boric and molybdic acids do not enter into complex formation.

2. A method is described whereby, through parallel series of measurements of solubility and of *p*H of the saturated solution of MoO_3 or WO_3 in solutions of sodium borate, carbonate and phosphate, respectively, the non-existence of boromolybdate ions and the existence of borotungstate ions in these solutions is demonstrated. The applicability of this method to other cases involving a change in solubility with attendant change in *p*H is suggested.

3. The solubilities of MoO_3 and of WO_3 have been determined at 28°.

4. The most satisfactory methods of preparation of pure MoO_3 and WO_3 are described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ROYAL VETERINARY AND AGRICULTURAL COLLEGE, COPENHAGEN]

Studies of Complex Formation between Aniline and Picrate Ion by Solubility Measurements

BY KAI JULIUS PEDERSEN

When aniline is added to a solution of a picrate the color changes from yellow to orange, showing that a complex is formed. In this paper the stability of the picrate–aniline complex in aqueous solution is determined from (1) the increase in solubility of anilinium picrate when aniline is added, and (2) the increase in solubility of aniline when sodium picrate is added. For comparison, the solubility of anilinium sulfate in aqueous solutions of aniline was also determined, and, finally, that of aniline in solutions of sodium benzoate, anilinium sulfate and potassium sulfate.

Materials

Aniline (Kahlbaum, pro analysi) redistilled, f. p. −6.2°.

Anilinium Picrate.—Two isomeric forms could be prepared from the solution: 35.6 g. of picric acid (pro analysi) dissolved in 1000 cc. of boiling water, and 14.4 g. of aniline added. If it was cooled quickly in ice water the crystals were small and light yellow with a tinge of green, indistinguishable from picric acid. This form could be recrystallized unchanged when dissolved in hot water and cooled quickly. If, however, the original solution or a warm solution of the light-colored form was cooled slowly, larger crystals of a stronger yellow color, like that of potassium picrate, were obtained. If the metastable form was left at room temperature with a little water it gradually transformed into the stable form. The resemblance of the two forms to picric acid and potassium picrate, respectively, is so striking that we may take it as a sign of similarity in molecular structure. The most obvious explanation, that the form which looks like picric acid is a molecular compound of this acid and aniline, does not seem to hold, because it has been found[1] that the color changes when organic nitro compounds form addition products with aromatic molecules. The solubility measurements were (with one exception) carried out with the stable form. This was first recrystallized twice from water.

Sodium Picrate.—The monohydrate was prepared from sodium carbonate and picric acid, both pro analysi; recrystallized once; dried in the air.

Anilinium Sulfate.—From aniline and sulfuric acid; recrystallized; dried *in vacuo* over concd. sulfuric acid.

Sodium Benzoate.—Solutions were prepared by neutralizing benzoic acid pro analysi with sodium hydroxide solution.

The saturated solutions were prepared in glass-stoppered bottles whose necks were covered with ground-on glass bells. The bottles were rotated in a water thermostat at 18.15°.

Samples of the saturated solutions of the two anilinium salts were sucked from the bottle, which was not taken from the thermostat, through a porous glass filter into a pipet. The anilinium ion was titrated with 0.025 *N* barium hydroxide or 0.1 *N* sodium hydroxide. Phenolphthalein was used as indicator. The end-point was distinct even in the yellow picrate solutions.

The solutions saturated with aniline were apt to form a rather stable suspension of aniline particles. However, when the sample was sucked into the pipet through a plug of cotton wool a clear solution was obtained. Usually 10 cc. was taken from the saturated solution and diluted to 100 cc. in a graduated flask; 10 cc. of this dilute solution was pipetted into a glass-stoppered bottle, and 5 cc. of 2 *N* potassium bromide and a small excess of 0.1 *N* potassium bromate (one mole of aniline uses 6 equivalents of bromate)

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[1] Pfeiffer, "Organische Molekülverbindungen," 1922, pp. 218–245.

were added. The solution was now acidified with 15 cc. of 2 N sulfuric acid and immediately stoppered and left in the dark for some minutes. A white precipitate of tribromoaniline is formed. Then 1 g. of potassium iodide was added, and the iodine set free titrated with thiosulfate. When the analysis is performed in this way an accuracy of ±0.1% may be obtained. It was found that the presence of benzoate or picrate in the solution does not interfere.

The Solubility of Anilinium Picrate

It was found necessary to use a rather large excess of crystals in order to attain equilibrium between crystals and solution quickly enough. First, all the anilinium picrate was rotated with pure water in the thermostat. Every day a sample was analyzed, and fresh water given to the crystals. The solubilities found increased slightly, but only about 0.1% per day. This increase is not due to incomplete saturation as may be seen from the following experiment. If we start with a supersaturated solution, made by shaking the crystals at a higher temperature before the rotation at 18.15°, the same solubility is found. For our purpose it was sufficient to make relative measurements, and the nature of this increase was therefore not further investigated. When the crystals had been rotated with water for a week they were sucked from the solution and dried. They were used for two series of experiments (Tables I and II) which were carried out simultaneously. For each series a bottle was charged with 10 g. of the crystals and 125 cc. of the first solutions given in the tables. One and two days later samples of 50 cc. were taken. The analyses usually agreed within 0.2%. The remaining solution was sucked from the crystals on a porous glass filter. They were washed with the solution given in the second line of the table, and rotated with 125 cc. of this solution. The experiments were continued in the same way until all the solutions had been examined. At the end the crystals were again rotated with the first solution. In both series the result was about 1% greater than the first time. The solubilities (s moles per liter), given in the second column of the tables, have all been referred to the time of the first determination by means of a small correction.

In the first series the solubility was determined in solutions of 0.00993 N hydrochloric acid containing from 0 to 0.08 M sodium chloride. At this hydrogen-ion concentration a small fraction of the picrate ion forms undissociated picric acid, while the anilinium ion does not give off protons. In the fourth column of Table I is given the dissociation constant K_c of picric acid, calculated from the empirical formula

$$\log K_c = 0.180 - 1 + 1.307 \sqrt[3]{\mu}$$

found by v. Halban and Ebert.[2] μ is the ionic strength of the solution. By means of K_c we calculate the concentration of undissociated picric acid (HPi), given in column 5, and $(\mathrm{Pi}^-) = s - (\mathrm{HPi})$. The solubility product $L = s(\mathrm{Pi}^-)$ may be expressed by the interpolation formula given at the bottom of the table. In the two last columns the values of $-\log L$ found directly from the measurements and calculated from the formula are compared.

TABLE I

SOLUBILITY OF ANILINIUM PICRATE IN 0.00993 N HYDROCHLORIC ACID CONTAINING FROM 0 TO 0.08 M SODIUM CHLORIDE AT 18.15°

(NaCl)	s	μ	K_c	(HPi)	(Pi^-)	$-\log L$	$-\log L_{\text{calcd.}}$
0.0000	0.01200	0.0216	0.350	0.00032	0.01168	3.853	3.853
.0100	.01234	.0320	.394	.00030	.01204	3.828	3.829
.0200	.01258	.0423	.431	.00028	.01230	3.810	3.811
.0400	.01297	.0627	.500	.00025	.01272	3.783	3.783
.0800	.01344	.1032	.621	.00021	.01323	3.750	3.746

$-\log L = 3.982 - \sqrt{\mu} + 0.82\mu.$

TABLE II

SOLUBILITY OF ANILINIUM PICRATE IN SOLUTIONS OF ANILINE AT 18.15°

$(\mathrm{An})_{\text{stoich.}}$	s	$-\log L$	(Pi^-)	$s - (\mathrm{Pi}^-)$	(AnPi^-)	$(\mathrm{An_2Pi}^-)$	(An)	$K_1 + K_2(\mathrm{An})$ exp.	$K_1 + K_2(\mathrm{An})$ calcd.
(0.0000	0.01176)								
.0513	.01225	3.880	0.01076	0.00149	0.00142	0.00007	0.0497	2.79	2.71
.0990	.01299	3.877	.01022	.00277	.00254	.00023	.0960	2.82	2.82
.1535	.01386	3.874	.00964	.00422	.00370	.00052	.1488	2.94	2.95
.2050	.01472	3.871	.00914	.00558	.00470	.00088	.1985	3.07	3.07
.2524	.01554	3.867	.00874	.00680	.00553	.00127	.2443	3.18	3.18

$K_1 = 2.590 \quad K_2 = 2.435$

In the second series (Table II) the solubility of anilinium picrate in solutions of aniline was determined. In the first column is given the stoichiometric concentration of aniline (free and complex, but not anilinium ion). In the second column is given the solubility s of anilinium picrate found by analysis. We shall see that we may explain the increase in solubility on adding

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[2] V. Halban and Ebert, *Z. physik. Chem.*, **112**, 380 (1924).

aniline by the assumption that a part of the picrate ions has formed complex compounds with aniline. This explanation is supported by the very distinct displacement of the color toward orange when aniline is added. We assume that no complex is formed between aniline and the anilinium ion (see below). In all the solutions the aniline concentration is so great that the anilinium ions have not given off hydrogen ions to any appreciable extent. We then have

$$(\mathrm{Pi}^-) = L/(\mathrm{AnH}^+) = L/s$$

where L may be calculated from the formula found in the first series. The concentration of complex picrate ion, $s - (\mathrm{Pi}^-)$, is given in the fifth column of the table. The simplest assumption is that only the complex AnPi^- is formed. Its stability is given by

$$K_1 = (\mathrm{AnPi}^-)/(\mathrm{An})(\mathrm{Pi}^-) \qquad (1)$$

However, we get the best agreement with the measurements of the solubility of aniline in sodium picrate solution (see later) if we assume that one more molecule of aniline may combine with the picrate ion to form the complex $\mathrm{An_2Pi}^-$. The stability of this complex may be expressed by

$$K_2 = (\mathrm{An_2Pi}^-)/(\mathrm{An})^2(\mathrm{Pi}^-) \qquad (2)$$

From formulas 1 and 2 and

$$(\mathrm{AnPi}^-) + (\mathrm{An_2Pi}^-) = s - (\mathrm{Pi}^-)$$

we find

$$K_1 + K_2(\mathrm{An}) = (s - (\mathrm{Pi}^-))/(\mathrm{An})(\mathrm{Pi}^-) \qquad (3)$$

The concentration of free aniline is

$$(\mathrm{An}) = (\mathrm{An})_{\mathrm{stoich.}} - (\mathrm{AnPi}^-) - 2(\mathrm{An_2Pi}^-) \qquad (4)$$

or approximately

$$(\mathrm{An}) = (\mathrm{An})_{\mathrm{stoich.}} - (s - (\mathrm{Pi}^-))$$

By means of formula 3 we calculate $K_1 + K_2$ (An), given in the last column but one of Table II. The values increase linearly with (An). If the medium change does not affect the constancy of K_1 and K_2 we find $K_1 = 2.590$ and $K_2 = 2.435$. The agreement with experiment is seen from the two last columns. When K_1 and K_2 are known we can calculate (AnPi^-) and $(\mathrm{An_2Pi}^-)$ from formulas 1 and 2. They are given in the sixth and seventh columns of the table. In the eighth column is given (An) calculated from equation 4.

One experiment was carried out with the light yellow, metastable form of anilinium picrate: 2 g. of the crystals was rotated with water at 18.15° and half an hour later the solubility 0.0148 *M* was found. A few strongly yellow crystals were already visible. One hour after the start the greater part of the crystals had been transformed. Now the solution above the crystals was 0.0138 *M*. The next day only the stable form was seen. The solubility 0.0116 was found. The experiment shows that the solubility of the metastable form is 28% (or possibly a little more) greater than that of the stable form.

Two determinations of the solubility of anilinium picrate in water are given in the literature. Smolka[3] found 0.45% (*i. e.*, 0.0140 *M*) at 17.5°, while Vignon and Évieux[4] found 0.54% (*i. e.*, 0.0168 *M*) at 22°. The values agree satisfactorily with the solubility of the metastable form found in this paper.

The Solubility of Anilinium Sulfate

Euler[5] has determined the solubility of aniline in different salt solutions. He found that, although it decreases on addition of most salts, it increases when anilinium salts are added. Also Sidgwick, Pickford and Wilsdon[6] found a very considerable rise in solubility when much chloride is added. Euler suggests the explanation that a complex between the anilinium ion and aniline is formed, but his experiments are not sufficient for proving it. It might be decided by examining the solubility of a sparingly soluble anilinium salt in solutions of aniline. Unfortunately most anilinium salts are easily soluble. Anilinium picrate has a very appropriate solubility, but, for obvious reasons, it cannot be used. Although a less soluble salt would be preferable, anilinium sulfate was chosen for the examination.

The solubility of anilinium sulfate in water containing from 0 to 0.29 *M* aniline is given in Table III. The hydrolysis of the salt has some influence on the solubility in pure water, while it is negligible for the solutions containing aniline. The solubility in water may be corrected for the hydrolysis in the following way. We denote by s the observed solubility, and by s' the solubility if the salt were not hydrolyzed. We have

$$4s'^3 = (2s - (\mathrm{An}))^2(s - (\mathrm{HSO_4}^-))$$

If we use the rough estimates (at the ionic strength 0.6)

$$(\mathrm{An})(\mathrm{H}^+)/(\mathrm{AnH}^+) = 2 \times 10^{-5}$$

and

$$(\mathrm{SO_4}^{--})(\mathrm{H}^+)/(\mathrm{HSO_4}^-) = 0.1$$

we find $(\mathrm{An}) = 0.0049$ and $(\mathrm{HSO_4}^-) = 0.0033$. Hence, $s' = 0.2011$.

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(3) Smolka, *Monatsh.*, **6**, 921 (1886).

(4) Vignon and Évieux, *Compt. rend.*, **147**, 67 (1908).

(5) Euler, *Arkiv f. Kemi, Mineralogi och Geologi*, **1**, 135 (1903); **6**, No. 14 (1917); *Z. Elektrochem.*, **23**, 192 (1917).

(6) Sidgwick, Pickford and Wilsdon, *J. Chem. Soc.*, **99**, 1122 (1911).

Inspection of Table III shows that addition of aniline has no appreciable effect on the solubility of anilinium sulfate. We may therefore conclude that no appreciable complex formation takes place.

TABLE III

SOLUBILITY OF ANILINIUM SULFATE IN AQUEOUS SOLUTIONS OF ANILINE AT 18.15°

(An)	Moles $(AnH)_2SO_4$ per liter of satd. soln.
0.0000	0.2038 (corrected for hydrolysis: 0.2011)
.0298	.2014
.1444	.2015
.2905	.2019

The Solubility of Aniline

As further test of the results found above the solubility of aniline was determined in solutions of sodium picrate, sodium benzoate, anilinium sulfate and potassium sulfate. Only a small excess of aniline was used, and it was shown that an increase in the amount used had no appreciable influence.

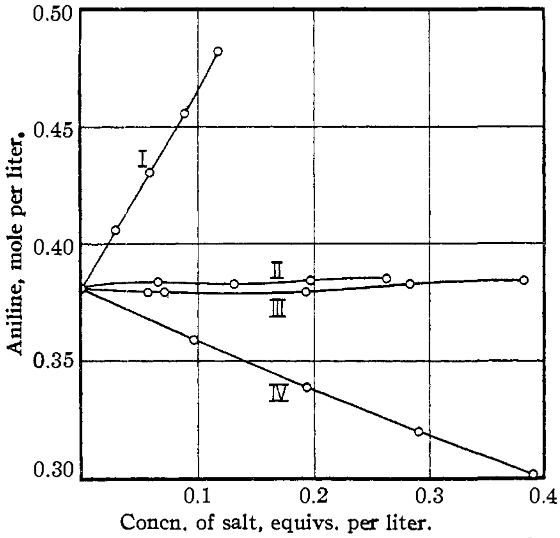

Fig. 1.—Solubilities of aniline in salt solutions: I, sodium picrate; II, sodium benzoate; III, anilinium sulfate; IV, potassium sulfate.

Tables IV and V and the figure contain the experimental data. The concentrations of the solvent salts given in the tables have been corrected for the dilution with the dissolved aniline on the assumption that this dissolves without change of volume. The solutions containing anilinium sulfate were analyzed for total aniline by the bromination method, and for anilinium ion by titration with sodium hydroxide. The solubility of aniline is the difference between the two results.

The first column of Table IV gives the stoichiometric concentration p of sodium picrate, the second the solubility s of aniline. The increase is great. In order to find the concentration of complex aniline we must know the salting-out effect on aniline. It is seen from Table V that sodium benzoate has a very small effect. From the similarity in structure of this salt and sodium picrate we may conclude that their salting-out effects are probably not much different. However, in the experiments more than half of the picrate ion has been transformed into complex ions. If we assume that they all have the same salting-out effect as the benzoate ion, we find the concentrations of free aniline given in the third column of Table IV.

TABLE IV

THE SOLUBILITY OF ANILINE IN SOLUTIONS OF SODIUM PICRATE AT 18.15°

p	s	(An)	Δs	$\Delta s/p$	s (calcd.)	Deviation, %
0.0000				0.745 (extrapolated)		
.0297	0.4058	0.3830	0.0228	.768	0.4046	0.3
.0594	.4303	.3832	.0471	.795	.4263	.9
.0889	.4554	.3832	.0722	.813	.4477	1.7
.1181	.4820	.3830	.0990	.839	.4688	2.7

TABLE V

THE SOLUBILITY OF ANILINE IN SOLUTIONS OF SODIUM BENZOATE, ANILINIUM SULFATE AND POTASSIUM SULFATE AT 18.15°

Sodium benzoate Salt mol. concn.	s	$(AnH)_2SO_4$ Salt mol. concn.	s	K_2SO_4 Salt mol. concn.	s
0.0000	0.3818	0.0000	0.3818	0.0000	0.3818
.0659	.3833	.0289	.3791	.0483	.3589
.1318	.3827	.0356	.3792	.0970	.3384
.1977	.3841	.0968	.3793	.1456	.3197
.2636	.3850	.0968	.3792	.1948	.3012
		.1417	.3829		
		.1910	.3836		
		.1912	.3839		

The concentration of complex aniline is $\Delta s = s - (An)$. If our conclusions from the solubility of anilinium picrate hold we have

$$p = (Pi^-) + (AnPi^-) + (An_2Pi^-)$$
$$\Delta s = (AnPi^-) + 2(An_2Pi^-)$$

and the equations 1 and 2, where K_1 and K_2 have the values found above. Hence we find

$$\frac{\Delta s}{p} = \frac{K_1(An) + 2K_2(An)^2}{1 + K_1(An) + K_2(An)^2} \qquad (5)$$

From this equation and the assumption that (An) is 0.383 throughout the series, we find, when $K_1 = 2.590$ and $K_2 = 2.435$ are introduced

$$\Delta s/p = 0.726$$

From the equations 1, 2 and 5 we also find that the following relations should hold for all the experiments in Table IV.

$(\mathrm{Pi}^-) = 0.426\,p \quad (\mathrm{AnPi}^-) = 0.422\,p \quad (\mathrm{An_2Pi}^-) = 0.152\,p$

As seen from Table IV $\Delta s/p$, given in the fifth column, increases when the concentration of picrate is increased. We may expect the best agreement at infinite dilution. If we extrapolate to $p = 0$ we find $\Delta s/p = 0.745$ which agrees satisfactorily with the value 0.726 calculated from the constants K_1 and K_2 found before. From the latter value we may calculate s given in the last column but one. The deviations from the experimental values are given in the last column.

The data in Table II gave no convincing proof of the existence of the complex with two molecules of aniline per picrate ion. The increase in $K_1 + K_2(\mathrm{An})$ is so small that it may possibly be explained by a medium effect, K_2 being zero. However, agreement between the data of Tables II and IV is only possible if we assume that the complex $\mathrm{An_2Pi}^-$ also exists. If this were not the case we would have instead of equation 5

$$\frac{\Delta s}{p} = \frac{K_1(\mathrm{An})}{1 + K_1(\mathrm{An})}$$

If we introduce the values $(\mathrm{An}) = 0.383$ and $\Delta s/p = 0.745$, found from the solubility of aniline, we obtain $K_1 = 7.64$, while from the solubility of anilinium picrate we find, on the assumption that $K_2 = 0$, $K_1 = 2.79$–3.18.

Pfeiffer[1] has discussed the theory of addition compounds of organic nitro compounds. He comes to the conclusion that they are formed by "a saturation of residuary affinities between nitro groups and unsaturated carbon atoms."

Although our experiments give no evidence of the existence of a complex between one picrate ion and three molecules of aniline, one corresponding to each nitro group, they do not exclude the possibility.

The solubility of aniline in solutions of anilinium and potassium sulfate is given in the last four columns of Table V, and shown in the graph. While the solubility is almost unchanged by addition of anilinium sulfate, potassium sulfate has a considerable salting-out effect. Although the difference between the effects of the potassium and anilinium ion is considerable, it is not so great that it may not be explained without assuming that complex compounds are formed.

I wish to express my thanks to the head of the laboratory, Professor N. Bjerrum, for the interest he has taken in my work.

Summary

Two forms of anilinium picrate were prepared, a metastable form which has the same color as picric acid, and a stable form with the same color as potassium picrate. The former is 28% more soluble in water at 18° than the latter.

Solubilities at 18° were determined for anilinium picrate and sulfate in aqueous solutions of aniline, and for aniline in aqueous solutions of sodium picrate, sodium benzoate, anilinium sulfate and potassium sulfate.

From the experimental data it is concluded that the picrate ion forms complexes with one and two molecules of aniline. The complexity constants, defined by equations 1 and 2, are $K_1 = 2.59$ and $K_2 = 2.44$.

No complex formation between aniline and the anilinium ion could be detected.

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