at 1×10^{-5} N for tetrabutylammonium perchlorate in benzene at 25°. For tetraethylammonium iodide the triple ion formation should take place at a lower concentration than for the above reported salts since such an effect increases with decrease in ion size. The solubilities here reported are of the order of 10^{-2} N in pure ethylene dichloride and 10^{-4} N in 35.5% ethylene chloride. Therefore, it seems likely that multiple ion formation exists in all the solutions studied; straight line extrapolation to pure benzene is justified if such conditions continue to exist down to a dielectric constant of 2.274. Extrapolation of Fig. 1 gives a solubility of 6.918×10^{-6} mole per liter for the solubility of tetraethylammonium iodide in benzene at 25°. At this solubility, triple ions may reasonably be expected to exist. Further evidence of ion association would be obtainable from studies of the effect of a common ion upon the solubilities reported in this paper. It is planned to study this as well as the solubility relation in solvents of higher dielectric constant.

Ricci and Davis[4] proposed an empirical equation to relate solubility to dielectric constant of the solvent which showed that a plot of log S against log D should be a straight line with a slope of three. This equation assumed that the Debye–Hückel limiting law applied and that the activity coefficient of an electrolyte at saturation is a constant independent of the dielectric constant of the solvent medium. They further showed that approximate equality of activity coefficients could be expected between solvent dielectric constants of 80 and 40. This, together with the evidence of triple ion formation, seems to indicate that a slope of 3 should not be expected with our data. The explanation of the slope of 5 of Fig. 1 will have to wait until more data are available.

The dielectric constant of benzene is 2.274 and log $D = 0.3568$. By extrapolation of Fig. 1, assuming a straight line relation, a value of log S of -1.160 is obtained. This gives 6.918×10^{-6} mole per liter for the solubility of tetraethylammonium iodide in benzene at 25°.

Summary

The solubility of tetraethylammonium iodide in pure ethylene dichloride and ethylene dichloride–benzene mixtures has been determined. A plot of log S *versus* log D follows closely a straight line with a slope of 5 in contrast to the value of 3 found in solvents with higher dielectric constant.

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[4] Ricci and Davis, THIS JOURNAL, **62**, 407 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF SANITARY ENGINEERING, HARVARD GRADUATE SCHOOL OF ENGINEERING]

Equilibrium Studies on N-Chloro Compounds. I. The Ionization Constant of N-Chloro-*p*-toluenesulfonamide[1]

BY J. CARRELL MORRIS, J. ALFREDO SALAZAR[2] AND MARGARET A. WINEMAN

The N-chloro compounds, those substances in which it may be considered that one or more chlorine atoms in the +1 oxidation state are bound to nitrogen, are of considerable interest because of the widespread use of a number of them as disinfecting agents. In many cases it is believed that their efficiencies as disinfecting agents are related to the magnitudes of their hydrolytic and other equilibrium reactions in water solution, but quantitative data on the equilibria with which disinfection results might be compared are available for only one or two isolated systems. The present series of papers is therefore concerned with the quantitative evaluation of equilibrium relationships for water solutions of certain important N-chloro compounds and with the use of the equilibrium constants so determined for predicting the disinfectant power of solutions of the N-chloro compounds under various conditions.

The system selected for primary study was that in which the substances Dichloramine-T, and Chloramine-T are participants. These two substances are, respectively, N,N-dichloro-*p*-toluenesulfonamide (I) and sodium N-chloro-*p*-toluenesulfonamide, the latter being the sodium salt of N-chloro-*p*-toluenesulfonamide (II). A number of equilibria are established in solutions of these materials, which can be described most conveniently in terms of the following processes:

I. The hydrolysis equilibrium for Dichloramine-T

$$\underset{\text{(I)}}{C_7H_7SO_2NCl_2} + H_2O = \underset{\text{(II)}}{C_7H_7SO_2NHCl} + HOCl \quad (1)$$

for which the equilibrium constant equation is[3]

$$K_h = \frac{(HOCl)(C_7H_7SO_2NHCl)}{(C_7H_7SO_2NCl_2)} \quad (1a)$$

II. The exchange or disproportionation reaction

$$\underset{\text{(II)}}{2C_7H_7SO_2NHCl} = \underset{\text{(I)}}{C_7H_7SO_2NCl_2} + C_7H_7SO_2NH_2 \quad (2)$$

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[1] This work was carried out under a research contract with the Office of the Quartermaster General, U. S. Army.

[2] Now with the West Virginia State Department of Health, Charleston, W. Va.

[3] In all of the equations of this paper parentheses, except when they are used just to set off mathematical terms, indicate molar activities of the substances concerned and square brackets indicate molar concentrations. For non-ionic substances the two are assumed to be the same within the experimental accuracy of the determinations.

with the equilibrium constant equation

$$K_d = \frac{(C_7H_7SO_2NCl_2)(C_7H_7SO_2NH_2)}{(C_7H_7SO_2NHCl)^2} \quad (2a)$$

III. The ionization of the hypochlorous acid produced in equation (1)

$$HOCl = H^+ + OCl^- \quad (3)$$

for which

$$K_1 = \frac{(H^+)(OCl^-)}{(HOCl)} \quad (3a)$$

IV. The ionization of N-chloro-p-toluenesulfonamide

$$C_7H_7SO_2NHCl = H^+ + C_7H_7SO_2NCl^- \quad (4)$$

giving an ionization constant

$$K_2 = \frac{(H^+)(C_7H_7SO_2NCl^-)}{(C_7H_7SO_2NHCl)} \quad (4a)$$

A fifth reaction, the acid ionization of $C_7H_7SO_2NH_2$ occurs under some conditions, and must eventually be included for a complete depiction of the system. However, preliminary studies indicate that the ionization constant is so small, perhaps 10^{-10}, that this reaction is a measurable factor only above pH 9. Other possible pertinent reactions, such as the hydrolysis of $C_7H_7SO_2NHCl$, need not be included, for they can be obtained by appropriate combination of the listed reactions.

The first two of these equilibria have been studied quantitatively by Soper.[4] By measuring the apparent solubility of Dichloramine-T[5] in 0.001 M H_2SO_4, by itself and in the presence of a known large excess of hypochlorous acid to repress the hydrolysis, he was able to calculate a value of 8.0×10^{-7} for K_h. The disproportionation constant, K_d, was evaluated, with the aid of the value for K_h, by measuring the apparent solubility of Dichloramine-T in 0.001 M sulfuric acid solutions containing known added amounts of p-toluenesulfonamide to displace reaction (2) to the left. These latter measurements have been repeated in connection with the present research and results in good agreement with the values given by Soper have been obtained. A combined average of the two sets of data yields $K_d = 6.1 \times 10^{-2}$.

The ionization constant for hypochlorous acid has been the subject of a number of studies which give as a probable best value $K_1 = 3.3 \times 10^{-8}$ at 25°.[6] The magnitude of this value is such that the ionization of hypochlorous acid did not occur to a measurable extent under the conditions of the present study, but it is concerned in the application of the results to disinfecting problems.

Although the compound $C_7H_7SO_2NHCl$ has not been isolated, its existence was demonstrated in Soper's studies and it is known that it must be a fairly strong acid because its sodium salt, Chloramine-T, gives only slightly basic solutions in water. However, no quantitative studies of the ionization constant have been reported. The simultaneous occurrence of the other listed equilibria and particularly of the disproportionation equilibrium introduces complicating factors into the standard procedures for determining ionization constants. In the present study these difficulties have been taken care of by appropriate mathematical treatment and the ionization constant has been determined in two ways: by measurement of the apparent solubility of Dichloramine-T in solutions buffered to pH 4.5 and containing known added amounts of p-toluenesulfonamide, and by potentiometric titration of solutions of Chloramine-T with standard hydrochloric acid.

Experimental

Reagents.—Purified Chloramine-T, furnished by the Monsanto Chemical Company, was recrystallized from distilled water under such conditions that only about 25% yield was obtained. The product was filtered with suction through a sintered-glass funnel and was dried at room temperature in a vacuum desiccator. The resulting product was the trihydrate, $NaC_7H_7SO_2NCl \cdot 3H_2O$, and was found to contain 12.56% Cl, the theoretical value being 12.58%.

Dichloramine-T was prepared by passing gaseous chlorine into water solutions of purified Chloramine-T and filtering out the precipitated Dichloramine-T with suction through a sintered-glass funnel. The material thus obtained was resuspended in a dilute chlorine solution (about 5 p. p. m.) agitated overnight and refiltered; this process was repeated two or three times to ensure complete removal of incompletely chlorinated products. After the final filtration the moist product was used for the solubility studies without drying.

The p-toluenesulfonamide was an Eastman Kodak Co. product, which was recrystallized from glacial acetic acid, filtered with suction through a sintered-glass funnel, washed several times with small quantities of cold water to remove adherent acetic acid and then dried in a vacuum desiccator over sulfuric acid. The recrystallized compound had a melting point of 137.0–137.5°.

Solubility Studies.—Samples of Dichloramine-T weighing 1–2 g. (several times the amount required for saturation) were placed in 500-ml. glass-stoppered Pyrex bottles and the bottles were then filled approximately three-quarters full with conductivity water. To these solutions were then added the desired amounts of p-toluenesulfonamide and either sufficient sulfuric acid to make the solutions 0.001 M in that reagent or a sufficient quantity of an equimolar solution of acetic acid and sodium acetate to give about 0.05 M concentration of each substance. The bottles were then stoppered and placed in a rotating frame in a constant-temperature water-bath held at 25.0 ± 0.2°. The rotation of the frame caused the bottles to be inverted about four times a minute. Samples were taken from the bottles at six to eight hour intervals by pressure filtration through a microfilter stick and were analyzed for their concentrations of oxidizing chlorine. The shaking and sampling procedures were continued until constant values for the apparent solubility of the Dichloramine-T were obtained. Constancy within the precision of the analytical determinations was generally obtained after about twenty-four hours of shaking and was maintained for at least forty-eight hours longer. Analyses for oxidizing chlorine were conducted by adding excess potassium iodide to the sample and titrating with 0.01 N sodium thiosulfate.

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[4] Soper, *J. Chem. Soc.*, **125**, 1899 (1924).

[5] The "apparent solubility of Dichloramine-T" is evaluated by determining that oxidizing chlorine in solutions in equilibrium with solid Dichloramine-T which is attributable to dissolved Dichloramine-T itself or which, existing in other forms, has been produced from Dichloramine-T by any of the previously listed reactions.

[6] See, for example, Ingham and Morrison, *J. Chem. Soc.*, 1200 (1933), and Hagisawa, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **19**, 1220 (1940). A complete summary of the data on this ionization constant is given in Final Report, Contract OEMcmr-251, Disinfection of Water and Related Substances, Dec. 31, 1945.

Titration Studies.—For these determinations accurately weighed samples of recrystallized Chloramine-T were dissolved in conductivity water to make solutions ranging in concentration from 0.01 to 0.08 *M*. The solutions were then titrated potentiometrically with 0.5 *N* hydrochloric acid, the *p*H after each addition being measured by means of a Beckman Model G *p*H meter equipped with glass and saturated calomel electrodes. The meter and electrodes were calibrated before and after each titration against solutions of potassium acid phthalate and of phosphate buffer mixture prepared from Bureau of Standards salts according to their directions. Since these calibrations checked within 0.02 *p*H unit, it is believed that *p*H measurements during the course of the titration were accurate to a similar figure. The amounts of hydrochloric acid added were measured with a calibrated 10-ml. Exax buret, so that volumes could be measured with a precision of 0.01 ml. The necessity for refilling the buret for volume readings greater than 10 ml. made the measurement of the larger volumes less precise, but this did not affect the experimental results since the factor limiting the accuracy of the results for all volume measurements greater than a few ml. was the determination of the *p*H.

Because of the slight solubility of Dichloramine-T in water, precipitation of this substance occurred during the titrations, the first permanent precipitate appearing after the addition of 1–2 ml. of hydrochloric acid. When additional amounts of hydrochloric acid were added to solutions containing the precipitate, particularly in those instances in which only a small amount of precipitate was present, the *p*H showed an initial decrease greater than expected and a following slow increase for a period as long as ten minutes before stabilization resulted. The total amount of this shift was generally about 0.1 *p*H unit. It is believed to have been caused by a temporary supersaturation of the solution with Dichloramine-T upon the addition of the hydrochloric acid followed by a slow precipitation to equilibrium saturation conditions. As the amount of precipitate in the solution increased, the time for stabilization decreased until at the equivalence point it was complete in less than a minute. In the range in which this phenomenon was exhibited *p*H readings were not recorded until equilibrium conditions had been attained and the *p*H readings were constant for several minutes.

An example of the curves obtained showing the typical features of the titrations is shown in Fig. 1. Section A of the curve shows the region in which the solution was not yet saturated with Dichloramine-T and was therefore clear. At the point corresponding to the addition of 1 ml. of hydrochloric acid a break in the curve is noted, coincident with the appearance of a precipitate of Dichloramine-T. The next three points, shown as section B, presumably correspond to a region of supersaturation with Dichloramine-T in which the supersaturation was being relieved so slowly that no drift in the *p*H values was observed. At the point corresponding to the addition of 2 ml. of hydrochloric acid a second break occurs, this being the first point for which the previously discussed shift in *p*H with time was observed. For the region beyond this, section C, the recorded points represent the *p*H readings obtained after stable conditions in the solution were attained and are assumed to correspond to an equilibrium saturation state for the Dichloramine-T present.

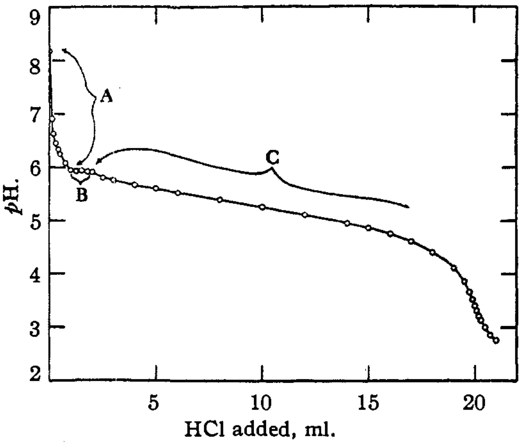

Fig. 1.—Titration of 0.0400 *M* Chloramine-T with 0.500 *M* HCl. Volume of solution 250 ml.: A, region with no precipitate, solution unsaturated with Dichloramine-T; B, region of supersaturation with Dichloramine-T; C, region with precipitate of Dichloramine-T in equilibrium with saturated solution.

The most concentrated solution titrated, 0.08 *M*, showed a fourth section just before the equivalence point. It was possible to calculate that in this region a large enough quantity of *p*-toluenesulfonamide had been produced to exceed its solubility, so that in this range both Dichloramine-T and *p*-toluenesulfonamide were being precipitated by the addition of further hydrochloric acid. This section was not used for any of the calculations.

Theory and Results

Solubility Studies.—In sufficiently acid solutions (0.002 *N*) of Dichloramine-T only the equilibria represented by reactions (1) and (2) are analytically significant, for the ionization of the weakly acidic compounds, hypochlorous acid and $C_7H_7SO_2NHCl$ is substantially completely repressed. Under these conditions the equivalents of oxidizing or "titratable" chlorine per liter, T_a, in the solution can be represented by the equation

$$T_a = 2[\text{HOCl}] + 2[C_7H_7SO_2NHCl] + 4[C_7H_7SO_2NCl_2] \quad (5)$$

When the concentration of titratable chlorine in acid solutions in equilibrium with an excess of solid Dichloramine-T, to which various amounts of *p*-toluenesulfonamide have been added, is measured, T_a is found to increase with increase in the concentration of added *p*-toluenesulfonamide because of the displacement of reaction (2) to the left. The accompanying decrease in the Dichloramine-T concentration is compensated for by additional solution of solid Dichloramine-T. On the assumption that the activity of the dissolved Dichloramine-T and hence its true solubility is constant regardless of the presence of the other dissolved substances and with a knowledge of the hydrolysis constant, K_h, it is possible to evaluate the disproportionation constant, K_d, from the increase in the titratable chlorine of the saturated solutions with increase of added *p*-toluenesulfonamide. This is the procedure which was followed by Soper.[4]

If the acidity at which these studies are carried out is changed to a *p*H of 4 to 5, the titratable chlorine level in the solution is further measurably increased over that obtained for the same concentration of added *p*-toluenesulfonamide in the more acid solutions because of the ionization of $C_7H_7SO_2NHCl$, which displaces reaction (2) even more to the left. At *p*H values less than 5 the ionization of hypochlorous acid is still not a factor. For solutions at *p*H 4 to 5 the equation for the equivalents of oxidizing chlorine in the saturated solutions becomes

$$T_b = 2[\mathrm{HOCl}] + 2[\mathrm{C_7H_7SO_2NHCl}] + 2[\mathrm{C_7H_7SO_2NCl^-}] + 4[\mathrm{C_7H_7SO_2NCl_2}] \quad (6)$$

Since the concentration of hypochlorous acid is negligibly small for solutions in which the added *p*-toluenesulfonamide is 0.001 *M* or greater, and since the concentration of dissolved $C_7H_7SO_2NCl_2$ may be considered to be constant, equations (5) and (6) may be reduced to the forms

$$T_a = T_2 + 2[\mathrm{C_7H_7SO_2NHCl}] \quad (7)$$

$$T_b = T_2 + 2[\mathrm{C_7H_7SO_2NHCl}] + 2[\mathrm{C_7H_7SO_2NCl^-}] \quad (8)$$

where T_2 is the saturation concentration of $C_7H_7SO_2NCl_2$ in equivalents per liter, determined by Soper to be 0.310×10^{-3}. Now if equations (7) and (8) be taken to apply to solutions to which the same number of moles, *N*, of *p*-toluenesulfonamide have been added per liter of solution, then the expressions for K_d for the two conditions may be written

$$K_d = \frac{(\mathrm{C_7H_7SO_2NHCl})^2}{(\mathrm{C_7H_7SO_2NCl_2})(\mathrm{C_7H_7SO_2NH_2})} = \frac{(T_a - T_2)^2}{T_2\left(N - \dfrac{T_a - T_2}{4}\right)} = \frac{(T_b - T_2 - 2[\mathrm{C_7H_7SO_2NCl^-}])^2}{T_2\left(N - \dfrac{T_b - T_2}{4}\right)}$$

the second term in the denominator of each expression being derived from the stoichiometry of reaction (2). Solution of these expressions for the concentration of $C_7H_7SO_2NCl^-$ yields the equation

$$[\mathrm{C_7H_7SO_2NCl^-}] = \frac{T_b - T_2}{2}\left(1 - \frac{T_a - T_2}{T_b - T_2}\sqrt{\frac{4N - T_b + T_2}{4N - T_a + T_2}}\right) \quad (9)$$

The ionization constant for $C_7H_7SO_2NHCl$ expressed in terms of the concentration of $C_7H_7SO_2NCl^-$ and the measured properties of the saturated buffer solutions is given by the following expression derived from equations (4a) and (8)

$$K_2 = \frac{(\mathrm{H^+})[\mathrm{C_7H_7SO_2NCl^-}]f}{{}^1/_2(T_b - T_2 - 2[\mathrm{C_7H_7SO_2NCl^-}])}$$

where *f* is the activity coefficient of the $C_7H_7SO_2NCl^-$ in the buffer solution. Substitution of equation (9) and simplification lead to the equation

$$K_2/f = (\mathrm{H^+})\left(\frac{T_b - T_2}{T_a - T_2}\sqrt{\frac{4N - T_a + T_2}{4N - T_b + T_2}} - 1\right) \quad (10)$$

Data obtained in the solubility studies and values of the term, K_2/f, calculated from them by means of equation (10) are shown in Table I. The ionic strength in these experiments, made up of the buffer ions and the ions produced in the reactions, was about 0.06.

Titration Studies.—If to a solution of $NaC_7H_7SO_2NCl$ of molar concentration *B*, is added a quantity of hydrochloric acid equivalent to a molar concentration *A*, both terms including a correction for the diluting effect of the added hydrochloric acid, then a simple application of equation (4) would indicate that the concentration of $C_7H_7SO_2NHCl$ formed is $A - [H^+]$, and that the remaining concentration of $C_7H_7SO_2NCl^-$ is $B - A + [H^+]$, where $[H^+]$ is the measured concentration of hydrogen ions in the solution after the addition of the acid. Then, by substitution of these quantities in the ionization constant equation, the constant might be calculated. Actually, because the $C_7H_7SO_2NHCl$ formed undergoes further reaction according to equation (2), this procedure overestimates the concentration of that substance and gives an apparent ionization constant considerably smaller than the true one. Two sets of calculations are necessary to correct for this additional reaction, one for the early part of the titration in which the solution is not saturated with respect to Dichloramine-T formed by reaction (2) and one for the later part in which the precipitation of Dichloramine-T has caused a further shift of reaction (2) to the right.

TABLE I

DETERMINATION OF THE IONIZATION CONSTANT FOR $C_7H_7SO_2NHCl$ FROM THE APPARENT SOLUBILITY OF DICHLORAMINE-T IN BUFFERED *p*-TOLUENESULFONAMIDE SOLUTIONS AT 25°

Added sulfonamide, moles/l. × 10^3	Saturation concentration, of oxidizing chlorine, equiv./l. × 10^3 in 0.001 *M* $H_2SO_4 = T_a$	in acetate buffer $= T_b$	*p*H of buffer solution	$K_2/f \times 10^6$
1.00	1.97	3.27	4.52	5.06
2.00	2.90	5.03	4.54	3.84
5.00	4.70	9.22	4.51	4.35
8.00	6.17	11.66	4.50	3.73
10.00	6.89	12.99	4.51	3.49
15.00	8.70	16.90	4.48	3.82

Average, excluding first value, 3.85

A. Region with no Precipitate of Dichloramine-T.—The term $A - (H^+)$ still represents the concentration of added acid which has reacted and so $B - A + [H^+]$ is still equal to the remaining concentration of $C_7H_7SO_2NCl^-$. However, $A - [H^+]$ is equal to the sum of the concentrations of the $C_7H_7SO_2NHCl$ and its subsequent reaction products. This may be expressed by the equation

$$A - [\mathrm{H^+}] = [\mathrm{C_7H_7SO_2NHCl}] + 2[\mathrm{C_7H_7SO_2NCl_2}] \quad (11)$$

Since the concentrations of $C_7H_7SO_2NCl_2$ and $C_7H_7SO_2NH_2$ formed by reaction (2) are equal, the equilibrium constant for the reaction may be written in the form

$$K_d = \frac{[\mathrm{C_7H_7SO_2NCl_2}]^2}{[\mathrm{C_7H_7SO_2NHCl}]^2} \quad (12)$$

from which

$$[\mathrm{C_7H_7SO_2NCl_2}] = \sqrt{K_d}[\mathrm{C_7H_7SO_2NHCl}] \quad (13)$$

Substitution in equation (11) and solution for the concentration of $C_7H_7SO_2NHCl$ gives

$$[\mathrm{C_7H_7SO_2NHCl}] = \frac{A - [\mathrm{H^+}]}{1 + 2\sqrt{K_d}} \quad (14)$$

This and the expression for the concentration of $C_7H_7SO_2NCl^-$, $B - A + [H^+]$, substituted in the ionization equation (4a) yield

$$K_2 = (1 + 2\sqrt{K_d})\,\frac{(H^+)(B - A + [H^+])f}{A - [H^+]} \qquad (15)$$

which, upon substitution of the value 0.061 for K_d, reduces to

$$K_2/f = 1.494\,\frac{(H^+)(B - A + [H^+])}{A - [H^+]} \qquad (16)$$

B. Region of Saturation with Dichloramine-T.—As soon as Dichloramine-T begins to precipitate, equations (11) and (12) are no longer true in terms of the dissolved Dichloramine-T concentration. However, the $C_7H_7SO_2NCl_2$ term in equation (11) may be replaced by $C_7H_7SO_2NH_2$, since this latter substance remains in solution, to give the modified equation

$$A - [H^+] = [C_7H_7SO_2NHCl] + 2[C_7H_7SO_2NH_2] \qquad (17)$$

Also, since the concentration of dissolved $C_7H_7SO_2NCl_2$ can now be considered constant at its molar solubility value, S, the disproportionation equation takes the form

$$K_d = \frac{[C_7H_7SO_2NH_2]S}{[C_7H_7SO_2NHCl]^2} \qquad (18)$$

Solution of equations (17) and (18) for the concentration of $C_7H_7SO_2NHCl$ gives

$$[C_7H_7SO_2NHCl] = \frac{S}{4K_d}\left[\left(\frac{8K_d(A - [H^+])}{S} + 1\right)^{1/2} - 1\right] \qquad (19)$$

Substitution of this expression and of $B - A + [H^+]$ for $[C_7H_7SO_2NCl^-]$ in the ionization constant equation (4a) gives

$$K_2/f = \frac{4K_d}{S}\,\frac{(H^+)(B - A + [H^+])}{\left(\frac{8K_d}{S}(A - [H^+]) + 1\right)^{1/2} - 1} \qquad (20)$$

Upon substitution of the numerical values, $K_d = 0.061$ and $S = 0.775 \times 10^{-4}$, equation (20) reduces to

$$K_2/f = \frac{3150(H^+)(B - A + [H^+])}{(6300\,(A - [H^+]) + 1)^{1/2} - 1} \qquad (21)$$

A typical example of the results obtained is shown in Table II, which gives the data obtained for a titration of 0.02 M Chloramine-T with 0.5 M hydrochloric acid, together with the ionization constants calculated from the data by means of equations (16) and (21) for the regions to which each is applicable. Table III presents a summary of the average ionization constants determined from this and the other titrations which were carried out. It is apparent from Table II that the calculated values of K_2/f showed a good constancy during the course of a titration and that satisfactory agreement between the constants for the region without precipitation and that with precipitation was obtained. The values calculated for the period before the beginning of precipitation are probably less reliable because of the greater errors involved in the measurement of the small amounts of acid added and also because the presence of very small amounts of acid or basic impurity in the Chloramine-T would have had a much more pronounced effect on the data in this region than in the later stages of the titration. On the other hand, because of the possible uncertainty as to the attainment of a constant equilibrium saturation concentration of Dichloramine-T during the latter part of the titrations, it is reassuring to have the values obtained foı the initial additions of HCl check the later ones so well.

TABLE II

TITRATION OF 0.02 M CHLORAMINE-T WITH HYDROCHLORIC ACID

500 ml. of 0.02000 M Chloramine-T titrated with 0.5000 N HCl; activity coefficient for H^+ in solution taken as 0.95

HCl added, ml.	pH	Concn. of added acid, A moles/l. $\times 10^{3a}$	$A - [H^+]$ $\times 10^3$	Unreacted $C_7H_7SO_2NCl^-$, $B - A + [H^+]$ $\times 10^{3a}$	K_2/f $\times 10^5$
A. No precipitate; equation 16 used for calculations					
0.00	7.68	0.000	0.000	20.00	..
.10	6.81	.100	.100	19.90	4.62[b]
.25	6.48	.250	.250	19.74	3.91[b]
.50	6.23	.500	.499	19.48	3.43
.75	6.04	.749	.748	19.22	3.50
1.00	5.92	.998	.997	18.96	3.41
1.25	5.82	1.247	1.245	18.70	3.39
1.50	5.73	1.496	1.494	18.45	3.43
2.00	5.61	1.992	1.989	17.93	3.31
B. Dichloramine-T precipitated, but not in equilibrium					
3.00	5.49	2.982	2.979	16.90	..
C. Solution saturated with Dichloramine-T; equation 21 used for calculations					
4.00	5.52	3.968	3.965	15.87	3.68
5.00	5.48	4.950	4.947	14.85	3.31
7.00	5.30	6.900	6.895	12.82	3.57
9.00	5.16	8.845	8.838	10.81	3.61
11.00	5.04	10.76	10.75	8.82	3.47
13.00	4.89	12.67	12.66	6.83	3.47
15.00	4.70	14.57	14.55	4.87	3.55
17.00	4.50	16.44	16.41	2.93	3.16
18.00	4.31	17.38	17.33	1.98	3.22
19.00	4.02	18.31	18.21	1.06	3.27
19.50	3.79	18.77	18.60	0.65	3.36
19.75	3.66	19.00	18.77	.47	3.27[c]
20.00	3.48	19.23	18.88	.35	3.66[c]
20.25	3.33	19.46	18.97	.25	3.69[c]
20.50	3.19	19.69	19.01	.20	4.07[c]
21.00	2.98	20.15	19.04	.15	4.96[c]
				Averages A	3.41
				C	3.42

[a] Corrected for dilution of sample by added hydrochloric acid. [b] Omitted from average because of lack of precision in volume of hydrochloric acid. [c] Omitted from average because of lack of precision in $B - A + [H^+]$ term.

In computing the term, $A - [H^+]$, it was necessary to convert the hydrogen ion activities calcu-

TABLE III

SUMMARY OF IONIZATION CONSTANT VALUES FOR N-CHLORO-*p*-TOLUENESULFONAMIDE OBTAINED BY TITRATION OF CHLORAMINE-T SOLUTIONS

Molar concn. of chloramine-T[a]	Section of titration curve and equation used	Average $K_2/f \times 10^5$	$-\log K_2/f$, pK_2'
0.01	A, equation 16	3.28	4.48
.01	C, equation 21	3.15	4.50
.02	A, equation 16	3.41	4.47
.02	C, equation 21	3.42	4.47
.04	A, equation 16	3.33	4.48
.04	C, equation 21	3.42	4.47
.08	A, equation 16	3.27	4.49
.08	C, equation 21	3.86	4.41

[a] This term also represents the ionic strength, μ, at which the titration was carried out.

lated from the *p*H measurements by the equation $pH = -\log(H^+)$ to hydrogen ion concentrations. The activity coefficients used for this purpose were taken from the chart of individual ion activities given by Chapin and Steiner.[7] The application of these corrections or the exact value of the activity coefficient used for them made very little difference over the greater part of the titration, but by including them it was possible to calculate consistent values for the ionization constant up to and even past the equivalence point.

In Fig. 2 a plot of the negative logarithms of K_2/f, pK_2' values, obtained in the various experiments against the square roots of the ionic strengths at which the experiments were conducted is shown, the circles having been drawn with radii corresponding to an error of 0.02 unit in *p*H measurement. The extrapolation line drawn through the points has a slope of 0.5, corresponding to that given by the simple Debye–Hückel expression in the form $pK_2 = pK_2' - 0.5\sqrt{\mu}$.

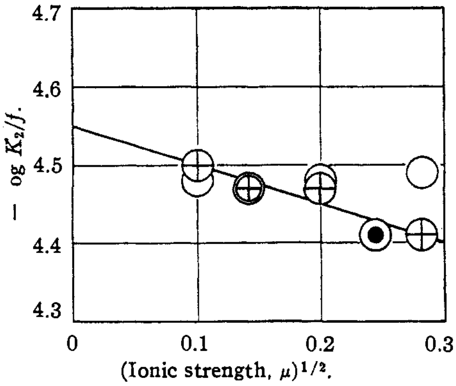

Fig. 2.—Variation of experimental ionization constants for $C_7H_7SO_2NHCl$ with ionic strength: ○, titration values for solutions unsaturated with Dichloramine-T; ⊕, titration values for solutions containing precipitate of Dichloramine-T; ◉, value from solubility studies. Line corresponds to equation $-\log f = 0.5\sqrt{\mu}$.

The value of pK_2 determined from the extrapolation is 4.55 ± 0.02. This leads to a value for K_2, the activity ionization constant of $C_7H_7SO_2NHCl$, of $2.8 \pm 0.2 \times 10^{-5}$.

Summary

The ionization constant for N-chloro-*p*-toluenesulfonamide has been determined by potentiometric titration of solutions of Chloramine-T with acid and by measurement of the solubility of Dichloramine-T in solutions at *p*H 4.5 containing added quantities of *p*-toluenesulfonamide. Suitable mathematical equations have been developed to overcome the complications caused by the simultaneous occurrence of other equilibrium processes along with the ionization equilibrium.

The value obtained for the activity ionization constant of $C_7H_7SO_2NHCl$ at 25° is $K_2 = 2.8 \pm 0.2 \times 10^{-5}$, corresponding to $pK_2 = 4.55 \pm 0.002$.

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(7) Chapin and Steiner, "Second Year College Chemistry," John Wiley and Sons, Inc., New York, N. Y., 5th edition, 1947, pp. 390–393.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Salts of an Aquoammonomolybdic Acid[1,2]

BY GEORGE W. WATT AND DARWIN D. DAVIES

In 1906, Rosenheim and Jacobsohn[3] prepared molybdenum(VI) oxide 3-ammonate by the interaction of the oxide and liquid ammonia. They considered the compound to be the diammonium salt of "imidomolybdic acid" and attempted to convert it to a lead(II) salt by reaction with lead(II) iodide in liquid ammonia at 108–109°, but their results were inconclusive.

In terms of Franklin's nitrogen system of compounds,[4] molybdenum(VI) oxide 3-ammonate may be looked upon as a salt of a mixed aquoammonomolybdic acid. As such, this acid salt should be unreactive toward liquid ammonia solutions of ammonium salts (acids in liquid ammonia), but in the same medium should react, for example, with potassium amide (a base in liquid ammonia) to form a tripotassium salt which in turn should be convertible by metathesis to other

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(2) Presented at the first Southwestern Regional Meeting of The American Chemical Society, Austin, Texas, December 7, 1945.

(3) Rosenheim and Jacobsohn, *Z. anorg. allgem. Chem.*, **50**, 297 (1906).

(4) Franklin, "The Nitrogen System of Compounds," A. C. S. Monograph No. 68, Reinhold Publishing Corporation, New York, N. Y., 1935, pp. 86–199.