701. *The Solvation of Ammonium Ions in Sulphuric Acid.*

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A method is described for the determination of the solvation number of the ammonium ion in ammonium sulphate–sulphuric acid–water mixtures based upon the direct dependence of the rate constant of cyclodehydration of 4-*p*-toluidinopent-3-en-2-one on the ratio of sulphuric acid to hydrogen sulphate (HSO_4) concentrations in the mixtures. The solvation number of one for the ammonium ion appears to be maintained up to 3M-concentration of ammonium sulphate in the presence of 2M-water.

A H_0 acidity scale is evaluated for the range of acid media investigated.

EVIDENCE that the ammonium ion in sulphuric acid has a solvation number of one has been provided by Gillespie *et al.*[1,2] by determinations of depression of freezing point of solutions of ammonium sulphate in nearly anhydrous sulphuric acid. It is assumed that solvation of the hydrogen sulphate anion is negligible and this view has been more fully discussed together with the effect of dissolved salts on the density and viscosity of sulphuric acid.[3] The highest concentration of ammonium sulphate employed in freezing-point determinations was 0·12M, but the probability that the solvation of the ammonium ion is maintained up to a 30-fold higher concentration has already been suggested by kinetic results obtained for the cyclodehydration of 4-*p*-toluidinopent-3-en-2-one to 2,4,6-trimethylquinoline in anhydrous ammonium sulphate–sulphuric acid solvents containing up to 4 moles/litre of the salt.[4] The mechanism of the cyclodehydration then suggested has since been slightly modified,[5] but the validity of the conclusion concerning the solvation

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[1] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.
[2] Gillespie and Oubridge, *J.*, 1956, 80.
[3] Gillespie and Wasif, *J.*, 1953, 215.
[4] Bonner, Thorne, and Wilkins, *J.*, 1955, 2351.
[5] Bonner and Barnard, *J.*, 1958, 4176.

of the ammonium ion is not affected. The unique value of the kinetic method is in allowing solvation studies at very much higher concentrations of the solute than is possible by freezing-point studies; in addition, it is evident that the method need not be confined to the anhydrous sulphuric acid media. This feature is important in that it provides a means of discovering whether or not the addition of water desolvates a cation in sulphuric acid. Accordingly, kinetic measurements have now been carried out in ammonium sulphate–sulphuric acid–water mixtures containing up to 3 moles per litre of ammonium sulphate and 2 moles per litre of water.

The interpretation of the results is based on the knowledge that, in the aqueous acid in the range 85—97% sulphuric acid, the kinetic results satisfy the relation[6] $\log k + H_0 =$ constant, where k is the rate constant of cyclodehydration for a given medium and H_0 is the corresponding value of the Hammett acidity function. Since an anil formed from primary aromatic amines and acetylacetone is almost certainly completely converted into its conjugate acid (AH^+) in these media,[5] it can be concluded that the cyclodehydration proceeds through a diprotonated form (AH_2^{++}) present in fractionally small amount. The equilibrium set up by these species can be represented by (1) The cyclodehydration

$$AH^+ + H_2SO_4 \rightleftharpoons AH_2^{++} + HSO_4^- \quad . \; . \; . \; . \; . \quad (1)$$

is a first-order reaction with a rate constant k_1 evaluated from (2), where [A] is the stoicheiometric concentration of the anil. The theoretical rate equation based on the Brönsted treatment is given by (3), in which k represents the product of the theoretical rate constant and the ratio of the activity coefficients of AH_2^{++} and the transition complex.

$$-d[A]/dt = k_1[A] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$-d[A]/dt = k[AH_2^{++}] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

If the anil is almost entirely present as its conjugate acid and $[AH^+] \gg [AH_2^{++}]$, equations (4) and (5) are obtained

$$k_1 = k[AH_2^{++}]/[AH^+] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$= kK[H_2SO_4]/[HSO_4^-] \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

where K represents the product of the thermodynamic equilibrium constant of eqn. (1) and the activity coefficient ratio $f_{AH^+}f_{H_2SO_4}/f_{AH_2^{++}}f_{HSO_4^-}$. Both k and K are assumed to be constant over the range of strongly acid media studied.

Two different sulphuric acid–water mixtures were investigated containing 97·90% and 98·44% of sulphuric acid severally, and in both cases the rate of cyclodehydration of 4-*p*-toluidinopent-3-en-2-one was measured in the presence of ammonium sulphate up to 3M-concentration. The ratio $[H_2SO_4]/[HSO_4^-]$ was calculated from the total weight of reactant solution (50 ml.) containing the ammonium sulphate at 25° before addition of the anil (*ca.* 0·5 g.). It was assumed that, in all media, the water present was quantitatively converted into hydroxonium and hydrogen sulphate ions. If the sulphuric acid molecules involved in solvation are effectively removed from participation in equilibrium (1), then the residual sulphuric acid concentration is reduced by n moles for each g.-ion of cation present with a solvation number of n. The calculated value of $[HSO_4^-]$ is independent of n, from which it follows that, if a direct dependence of k_1 on the ratio $[H_2SO_4]/[HSO_4^-]$ expressed in eqn. (5) is found for any one value of n, the experimental results cannot satisfy any other value of n. Three possibilities for cation solvation were considered, based on the following solvation numbers: (*a*) ammonium ion, 1; hydroxonium ion, 0; (*b*) ammonium ion, 1; hydroxonium ion, 1; and (*c*) ammonium and hydroxonium ions both zero. The calculated values of $[H_2SO_4]/[HSO_4^-]$ for each of these three cases are

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[6] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; Hammett and Paul, *ibid.*, 1934, **56**, 830.

designated *A*, *B*, and *C* respectively in the Table. The results previously reported[4] for pure sulphuric acid were recalculated, account being taken of the subsequent discovery[5] that the dissolved anil is almost completely converted into its conjugate acid by an equimolecular quantity of sulphuric acid with the formation of hydrogen sulphate ion. It is evident that equation (5) is only satisfied by the first proposition (*a*). The values of log(A/k_1) for this case are constant within each of the three media, and the mean values 1·66, 1·68, and 1·70 for these media are in good agreement. No constancy is apparent in the case of (*b*) or (*c*). The value of one for the solvation number of the hydroxonium ion was suggested on the basis of cryoscopy data on sulphuric acid solutions, but later work[3] on the molal volumes of these solutions has led to a revised value of 0·4. A recalculation of (*b*) with this value instead of unity gave a smaller but still significantly pronounced variation in the log ratio (from 1·72 to 1·56 in 97·9% sulphuric acid, and 1·77 to 1·61 in 98·44% sulphuric acid). It is possible that the hydroxonium ion is desolvated as the concentration of ammonium ion is increased, so that the values of *B* gradually approach those of *A*. In the absence of ammonium sulphate the log ratio $[H_2SO_4]/[HSO_4^-]$ in 97·9% sulphuric acid changes from 1·68 to 1·72 for a change of solvation number of the hydroxonium ion from 1 to 0·4, and the difference in the value of the log ratio is even less in 98·44% sulphuric acid. The possibility of desolvation of the ammonium ion in changing from pure sulphuric acid to aqueous acids containing up to 2M-water is clearly inadmissible. The fact that the relation between the ratio $[H_2SO_4]/[H_2O]$ and k_1 continues to hold up to a concentration of 3M-ammonium sulphate in the aqueous media suggests that the solvating power of the sulphuric acid is unimpaired by the presence of the water. This has a bearing on the problem of why the rate of nitration of aromatic compounds by the nitronium ion initially increases as water is added to pure sulphuric acid, in spite of accompanying decrease in the acidity of the medium.[8] In a discussion of this problem,[9] the explanation put forward, that the solvating power of the medium decreased on addition of water with a consequent decrease of energy of activation of the nitration reaction, now seems less acceptable than the alternative description which the authors provide by

Correlation of the rate constant k, and the ratio $[H_2SO_4]/[HSO_4^-]$ *for the cyclodehydration of* 4-p-*toluidinopent*-3-*en*-2-*one*.

Initial concn. of 4-toluidinopent-3-en-2-one, 0·05M; Temp. 25°.

	Stoicheiometric concn.							
H_2SO_4 (%)	$[(NH_4)_2SO_4]$ (M)	$[H_2SO_4]_T$ (M)	$[H_2O]$ (M)	10^3k_1 (min.$^{-1}$)	og A/k_1	log B/k_1	log C/k_1	$-H_0$
97·9	0	18·29	2·14	131	—	1·68	1·75	9·24
,,	1	17·13	2·00	68	1·65	1·57	1·73	8·84
,,	2	15·78	1·83	27	1·69	1·58	1·87	8·49
,,	3	14·36	1·68	10·4	1·65	1·38	2·08	8·04
98·4	0	18·46	1·59	165	—	1·75	1·79	9·39
,,	0·5	17·76	1·53	116	1·70	1·65	1·72	9·13
,,	1	17·08	1·48	76	1·67	1·62	1·73	8·92
,,	1·5	16·55	1·43	47	1·70	1·64	1·81	8·74
,,	2	15·87	1·37	35	1·66	1·58	1·82	8·56
,,	3	14·52	1·25	125	1·66	1·51	2·05	8·13
100	1	17·32	—	131	1·71	—	1·78	9·21
,,	2	16·04	—	55·4	1·65	—	1·80	8·76
,,	2·5	15·37	—	31·4	1·69	—	1·90	8·56
,,	3	14·70	—	17·2	1·73	—	2·05	8·34
,,	4	13·26	—	2·98	1·71	—	2·59	7·56

$A = [H_2SO_4]/[H_2O]$, monosolvation of the NH_4^+ ion only being assumed.
$B =$,, ,, ,, both NH_4^+ and H_3O^+ ions being assumed.
$C =$,, no solvation of either NH_4^+ of H_3O^+ ions being assumed.

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[7] Gillespie, *J.*, 1950, 2493.

[8] Martinsen, *Z. phys. Chem.*, 1904, **50**, 385; Bonner, James, Lowen, and Williams, *Nature*, 1949, **163**, 955.

[9] Gillespie and Norton, *J.*, 1953, 971.

applying the theory of solvent effects [10] to this medium in which addition of water produces a decrease in dielectric constant.

It is significant that it has been found previously [4,5] that log k_1 bears a linear relationship both to log $[H_2SO_4]/[HSO_4^-]$ and to $-H_0$ and that in each case the slope of the line is approximately -1. This indicates that values of H_0 for these sulphuric acid–ammonium sulphate–water mixtures parallel those of log $[H_2SO_4]/[HSO_4^-]$ and could be derived from them by the addition of a constant term, as in equation (6). Evaluation of the ratio

$$H_0 = \text{constant} - \log([H_2SO_4]/[HSO_4^-]) \quad . \; . \; . \; . \; . \quad (6)$$

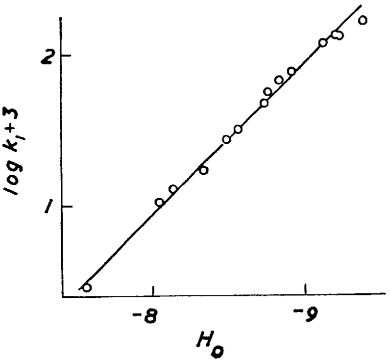
$[H_2SO_4]/[HSO_4^-]$ is based solely on the composition by weight of the mixtures and the assumption that there is complete conversion of the water present into hydroxonium ion and of the ammonium sulphate into the monosolvated ammonium ion, both species providing the corresponding quantity of hydrogen sulphate anion; if the stoicheiometric concentrations of sulphuric acid, water, and ammonium sulphate are represented by M, m_1, and m_2, respectively, it can be shown that the ratio is given by equation (7),

$$[H_2SO_4]/[HSO_4^-] = m - 1 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

where

$$m = (M - m_2)/(m_1 + 2m_2) \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

Brand [11] has already shown that, in the range 89—99·8% sulphuric acid, H_0 can be calculated from an equation of the type (6), in which the empirical constant is $-8{\cdot}36$.



With this constant, H_0 values have now been calculated for all media included in the Table, the equation being used in its more general form (9).

$$H_0 = -8{\cdot}36 - \log(m - 1) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

Values of H_0 are given in the last column of the Table. The plot of log k against $-H_0$ for these results is shown in the Figure. The slope of the straight line obtained is almost exactly unity as required by theory. The assumption that sulphuric acid molecules involved in solvation in solutions of high acidity are effectively removed from participation in equilibrium (1) and hence make no contribution to the acidity function, H_0, has some similarity to the contention [12] that in more aqueous sulphuric acid–water mixtures the water molecules involved in hydration of hydrogen ions do not contribute to the activity of the water present in these media.

Until further results are available, it cannot be assumed that the evaluation of H_0 for the sulphuric acid–ammonium sulphate–water system by means of equation (9) can be extended to media more aqueous than those here examined. Its importance, however,

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[10] Hughes and Ingold, *J.*, 1938, 244; Ingold, "Structure and Mechanism in Organic Chemistry," Bell & Sons, Ltd., London, 1953, p. 345.

[11] Brand, *J.*, 1950, 1002.

[12] Bascombe and Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158; Wyatt, *ibid.*, p. 162.

is that within the range of compositions studied it covers a scale of acidity in H_0 units equal to that extending from 85% to 98% sulphuric acid.

Considerable difficulty might arise in attempting to measure H_0 by the usual method [6] of determination of the extent of ionisation of an indicator B to its conjugate acid BH^+, because of the shift of spectrum which would be likely to occur with increasing concentration of ammonium sulphate.

In the above evaluation of the H_0 acidity scale, it is assumed that any substrate is present in such low concentrations that it has a negligible effect on the concentration of either sulphuric acid or hydrogen sulphate ion. Any appreciable change in these concentrations due to the added substrate would necessitate appropriate correction of the H_0 values indicated.

Experimental.—Materials and media. Sulphuric acid solutions were prepared and standardised as reported previously.[4] 4-*p*-Toluidinopent-3-en-2-one was crystallised from light petroleum (b. p. 40—60°) and had m. p. 68°.

Kinetic measurements. The ammonium sulphate (" AnalaR ") was weighed into a tared 50 ml. volumetric flask, the sulphuric acid medium added, and after dissolution of the salt, the solution was made up to the mark at 25°. The flask was reweighed and then drained into a 100 ml. reaction vessel having a B24 neck. The residue (0·5 ml.) which remained in the 50 ml. flask was neglected. *p*-Toluidinopent-3-en-3-one (0·47 g.) was weighed into a B24 cap which fitted to the reaction vessel. Zero time was taken from the moment when vigorous shaking was started to effect dissolution of the anil in the medium. Solution was complete in *ca.* 1—2 min.; 2 ml. samples were withdrawn at appropriate intervals of time and run into 20 ml. of water. The acetylacetone liberated from the residual anil was determined as previously described.[5]

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