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THE ACTIVITY COEFFICIENTS OF THE NON-IONIZED FORM OF SOME ACID INDICATORS

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Abstract—An equation has been derived for determining the activity coefficient "f_B" of a non-ionized form from the solubility and distribution coefficient for a case when the substance studied is in two forms only: non-ionized "B" and ionized "BH^+". The Hammett relation is shown to be valid also for solutions containing almost completely ionized species (indicators). The activity coefficients "f_B" for *o*- and *p*-nitroaniline and diphenylamine in aqueous H_2SO_4 solutions were measured. It was concluded from the results and also from published data that the Hammett acidity "h_0" is equal to the thermodynamic activity of protons.

AN interpretation of the kinetic data on reactions in solutions is difficult on account of the lack of information concerning the dependence of the activity coefficients of the non-ionized particles and ions on the solvent composition.

The acidity function $H_0 = -\lg (f_B/a_{H^+}f_{OH^+})$ which is used for interpretation of kinetic data comprises the ratio of the activity coefficients of the non-ionized f_B and ionized indicator forms f_{BH^+}. Elucidation of the dependence of f_B upon acid concentration should clarify the physical meaning of the concept of acidity. Boyd[1] found that the f_B values for nitroanilines, used in the measurement of h_0, do not remain constant with the variation of sulphuric acid concentration. This paper is an attempt to throw light on how the activity coefficients f_B of some indicators, differing in chemical structure, vary with the strength of sulphuric acid. Overlapping indicators for which the Hammett[2] relationship holds good were investigated.

In the measurement of activity coefficients from solubility or distribution coefficient the substance studied is assumed to be present in the acid solution in a single form corresponding in composition either to the solid phase or to the dissolved substance in the inert solvent used for the measurement of the activity coefficient. The activity coefficients obtained from such data are gross-values reflecting variation of the properties of the dissolved substance as a whole. In many cases, however, variations in the solvent composition, for instance, in acid concentration, result in the appearance of new forms of the dissolved substance. They may be ions, ion pairs, complexes, dimers, etc. In such cases the dependence of solubility or distribution coefficient on the solvent composition will reflect the variation of the activity coefficients and of the relative concentrations of those forms. For the indicators used in plotting "h_0" the basicity constants are known. In aqueous solutions of strong acids they are present as two equilibrium forms, non-ionized "B" and ionized "BH^+". This enables the activity coefficients "f_B" to be determined directly according to the concentration of the acid.

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[1] R. H. Boyd, *J. Amer. Chem. Soc.* **85**, 1555 (1963).

[2] L. P. Hammett, *Physical Organic Chemistry*. McGraw-Hill, N.Y. (1940).

Consider saturated "B" indicator solutions in the aqueous solutions of a strong acid and assume that the indicator is present in the acid only in two forms "B" and "BH^+" and that the composition of the solid phase is independent of the concentration of the acid which is in equilibrium with it. The concentration of the indicator must be much less than that of the acid, lest the properties of the acid medium should change.

The concentration of the substance investigated in the saturated solution is $S = C_B + C_{BH^+}$; B and BH^+ concentrations are interrelated by the equilibrium constant

$$\frac{C_B}{C_{BH^+}} = \frac{K_{BH^+}}{h_0}.$$

In the case of indicators, C_B and C_{BH^+} can be determined spectrophotometrically.

The precipitate is a non-ionized form and is in equilibrium with the non-ionized form "B" in the solution. The latter is in equilibrium with the "BH^+" form:

$$B_{solid} \rightleftarrows B;$$
$$B + H^+ \rightleftarrows BH^+.$$

In equilibrium the chemical potentials of the solid phase, μ_{solid}, and of the non-ionized form, μ_B, are equal. If the solid phase is chosen as a standard state, then μ_0 is similar for all phases:

$$\mu_0 + RT \ln a_{solid} = \mu_0 + RT \ln a_B;$$
$$a_{solid} = a_B = f_B \, . \, C_B.$$

The solid phase activity is constant. On the acidity scale f_B is usually assumed to be equal to unity in water. In that case a_{solid} is numerically equal to the solubility of the substance investigated in water S_0. Such a choice of the scale of relative units for f_B is justified for substances which are present in water in a single form. The saturated solution concentration S can be expressed through "h_0" and the basicity constant through K_{BH^+}:

$$S = C_B + C_{BH^+} = C_B \left(1 + \frac{h_0}{K_{BH^+}}\right).$$

The activity coefficient f_B in the acid investigated is equal to the ratio of the concentration of the saturated solution in water to that of the non-ionized form in the acid:

$$f_B = \frac{S_0}{C_B} = \frac{S_0}{S}\left(1 + \frac{h_0}{K_{BH^+}}\right).$$

If the solubility of the substance studied is high, the activity coefficient can be measured from the distribution coefficient $\gamma = C_a/C_i$ are concentrations of the substance in the acid and inert-solvent layer, respectively. In the inert layer the substance investigated is entirely in the "B" form. Neither acid nor water would be extracted into this layer. In equilibrium $a_i = a_B$ or $C_i \, . \, f_i = C_B \, . \, f_B$. In that case too f_B in water is assumed to be equal to unity. The coefficent of indicator distribution between the water and the inert solvent, γ_0, is equal to the activity coefficient, f_i, of the substance in the inert layer. The concentration of the substance in the acid layer is equal to the sum of concentrations of the B and BH^+ forms:

$$C_a = C_B + C_{BH^+}.$$

Then

$$\gamma = \frac{C_a}{C_l} = \frac{C_B + C_{BH^+}}{C_l} = \frac{C_B}{C_l}\left(1 + \frac{h_0}{K_{BH^+}}\right).$$

On the other hand,

$$\frac{C_B}{C_l} = f\frac{f_l}{f_B} = \frac{\gamma_0}{f_B}.$$

Consequently,

$$f_B = \frac{\gamma_0}{\gamma}\left(1 + \frac{h_0}{K_{BH^+}}\right)$$

EXPERIMENTAL TECHNIQUE

The solubility and distribution coefficients were measured spectrophotometrically. All experiments were run at 25 ± 0·1°. Saturated solutions and the mixtures of acid and organic solvent were kept in the thermostat for several hr, being continuously stirred.

The optical density of saturated solutions and of both two-phase system layers was measured in thermostated quartz cuvettes using a CΦ-4 spectrophotometer. The indicator concentrations in the measurements never exceeded 10^{-3} mol/lit. For such concentrations Lambert's law was found to be valid. The measurements were made in the maximum of the absorption band corresponding to the non-ionized form. The dependence of the molar absorption coefficient on the acid concentration was obtained for each indicator. CCl_4 was used as inert solvent in the measurement of the distribution coefficient. Prior to experiments all substances were subjected to purification by double recrystallization The m.ps were in agreement with the published data.[3] H_2SO_4[4] and CCl_4 were purified by distillation.* Aqueous solutions of H_2SO_4 were prepared by diluting 98·5% H_2SO_4 with twice distilled water. Concentration of the initial acid was determined from electric conductivity.[5]

EXPERIMENTAL DATA

The activity coefficients, f_B, of *p*- and *o*-nitroanilines and diphenylamine in aqueous solutions of H_2SO_4 were measured from the solubility and the distribution coefficients. Molar absorption coefficients "ε" were measured for these substances for a wide range of H_2SO_4 concentrations. The results obtained are presented in Tables 1–8 and in Fig. 1. The optical density of *p*-nitroaniline was measured at $\lambda = 380$ mμ, which corresponds to the non-ionized form absorption maximum. pK_{BH^+} is constant in the range from dilute solutions and up to 34·6% H_2SO_4 by wt (see Table 1). The average value of pK_{BH^+} is +0·99. Given in Tables 2 and 3 are *p*-nitroaniline values computed from the data on solubility and distribution coefficients, ranging from dilute solutions up to 30·4% H_2SO_4 by wt. The optical density of *o*-nitroaniline was measured at $\lambda = 410$ mμ, at the maximum of its non-ionized form. From pure water to 34·8% the average value of pK_{BH^+} is −0·33; in stronger solutions $pK_{BH^+} = -0{\cdot}29 \pm 0{\cdot}06$. Variation of pK_{BH^+} in this range is obviously due to inaccurate measurements, because the ratio C_{BH^+}/C_B is high (Table 4). Presented in Tables 5 and 6 are the f_B values obtained from the solubility and distribution coefficients over the range from pure water to 62·6% H_2SO_4 by wt. The measurements for diphenylamine were made at $\lambda = 280$ mμ, at the absorption maximum of its non-ionized form. The basicity constant K_{BH^+} is practically invariable from pure water to 30·9% H_2SO_4 by wt (Table 7). The average value of pK_{BH^+} is 0·71. Given in Table 8 are the activity coefficients f_B of diphenylamine in water and in acid solutions up to 30·6% H_2SO_4. The f_B values cited in the Tables were obtained from the Lit.[1a] Shown in Fig. 1 is the dependence of f_B on the strength of the acid for the 3 indicators. The coincidence of the f_B values computed from the solubility and distribution coefficients indicates that the composition of the solid phase did not vary with increasing acid concentration. The solubility of *p*- and *o*-nitroanilines in acids containing over

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* Note: In contrast to the technique described[4] H_2SO_4 was distilled only once.

[3] *Dictionary of Organic Compounds*. London (1946).

[4] N. G. Zarakhani and M. I. Vinnik, *Zh. Fiz. Khim.* 37, 3, 503 (1963).

[5] R. J. Gillespie, E. A. Robinson and C. Solomons, *J. Chem. Soc.* 4320 (1960); S. J. Bass, R. J. Gillespie, E. A. Robinson, *Ibid.* 821 (1960).

30% H_2SO_4 by wt is high. The indicator being completely ionized, the acidity of the medium at high solubilities is found to diminish perceptibly. To compute f_B in such cases, it is necessary to measure H_0 of the solutions. Correct values of f_B are obtained from the distribution coefficient, since they have been obtained for strong acid solutions, where the concentration of the indicator in the acid is within 0·1 mol/lit.

TABLE 1. MOLAR: ABSORPTION COEFFICIENT AT λ = 380 mμ OF *p*-NITROANILINE IN AQUEOUS SOLUTIONS OF H_2SO_4

% H_2SO_4 by wt 1	$\varepsilon \frac{1}{\text{Mol cm}}$ 2	$\lg \frac{C_B}{C_{BH^+}}$ 3	H_0 4	pK_{BH^+} 5
0·00	1·60 . 10^4	—	—	—
1·32	5·56 . 10^3	−0·28	+0·72	+1·00
2·02	3·99 . 10^3	−0·47	+0·52	+0·99
2·75	3·03 . 10^3	−0·64	+0·33	+0·97
3.52	2·3 . 10^3	−0·84	+0·14	+0·98
4·33	1·89 . 10^3	−0·88	+0·11	+0·99
4·88	1·66 . 10^3	−0·95	+0·05	+1·00
5·35	1·48 . 10^3	−1·00	−0·01	+0·99
5·86	1·36 . 10^3	−1·04	−0·07	+0·97
6·34	1·22 . 10^3	−1·10	−0·12	+0·98
6.94	1·09 . 10^3	−1·16	−0·17	+0·99
7·65	9·24 . 10^2	−1·25	−0·24	+1·01
8·35	8·35 . 10^2	−1·30	−0·31	+0·99
9·23	7·15 . 10^2	−1·37	−0·37	+1·00
9·99	6·34 . 10^2	−1·43	−0·43	+1·00
10·8	5·66 . 10^2	−1·48	−0·49	0·99
12·4	4·45 . 10^2	−1·60	−0·61	+0·99
13·7	3·78 . 10^2	−1·68	−0·71	+0·97
15·2	3·00 . 10^2	−1·79	−0·80	+0·99
17·1	2·48 . 10^2	−1·89	−0·92	+0·97
17·9	2·17 . 10^2	−1·96	−0·97	+0·99
19·9	1·76 . 10^2	−2·07	−1·10	+0·97
20·9	1·59 . 10^2	−2·13	−1·17	+0·96
21·8	1·41 . 10^2	−2·20	−1·23	+0·97
22·6	1·31 . 10^2	−2·25	−1·29	+0·96
23·4	1·17 . 10^2	−2·32	−1·35	+0·97
24·2	1·06 . 10^2	−2·39	−1·40	+0·99
24·7	1·03 . 10^2	−2·41	−1·44	+0·97
25·1	9·86 . 10^1	−2·44	−1·47	+0·97
26·1	9·03 . 10^1	−2·51	−1·54	+0·97
27·2	8·29 . 10^1	−2·58	−1·62	+0·96
28·3	7·60 . 10^1	−2·65	−1·70	+0·95
29·5	6·86 . 10^1	−2·75	−1·78	+0·97
29·7	6·60 . 10^1	−2·80	−1·80	+1·00
30·6	6·24 . 10^1	−2·86	−1·86	+1·00
31·4	5·99 . 10^1	−2·91	−1·92	+0·99
32·2	5·61 . 10^1	−3·01	−1·98	+1·03
33·2	5·29 . 10^1	−3·11	−2·05	+1·06
33·9	5·07 . 10^1	−3·19	−2·10	+1·09
34·6	4·80 . 10^1	−3·32	−2·16	+1·16

Note: $\lg (C_B/C_{BH^+})$ was computed from the values of absorption coefficients for the non-ionized form ε_B = 1·60 . 10^4 (1/Mole cm) and for the ionized form ε_{BH^+} = 40·4 (1/Mole cm) at λ = 380 mμ. The h_0 values were borrowed taken from the Lit.[13]

TABLE 2. SOLUBILITY OF *p*-NITROANILINE AND ITS ACTIVITY COEFFICIENTS f_B IN AQUEOUS SOLUTIONS OF H_2SO_4

% H_2SO_4 by wt	$S \frac{\text{Mole}}{\text{litre}}$	H_0	f_B
0·0	$3{\cdot}14 . 10^{-3}$	—	1·00
9·8	$8{\cdot}86 . 10^{-2}$	−0·42	0·95
14·9	$1{\cdot}69 . 10^{-1}$	−0·79	1·14
19·8	$3{\cdot}23 . 10^{-1}$	−1·08	1·15
20·0	$3{\cdot}28 . 10^{-1}$	−1·10	1·19
24·8	$4{\cdot}36 . 10^{-1}$	−1·46	—
29·7	$4{\cdot}97 . 10^{-1}$	−1·80	—
33·9	$6{\cdot}41 . 10^{-1}$	−2·10	—
34·0	$6{\cdot}38 . 10^{-1}$	−2·11	—

Note: Owing to high solubility the data for 24·8 %–34 % H_2SO_4 cannot be used for f_B computations.

TABLE 3. THE *p*-NITROANILINE ACTIVITY COEFFICIENTS f_B AS MEASURED FROM THE DISTRIBUTION OF THE SUBSTANCE BETWEEN THE ACID AND CARBON TETRACHLORIDE LAYERS

% H_2SO_4 by wt	f_B
0·0	1·00
21·4	1·24
23·7	1·17
30·4	1·27

TABLE 4. MOLAR ABSORPTION COEFFICIENT OF ORTHONITROANILINE AT $\lambda = 410\ m\mu$ AND $\lg(C_B/C_{BH^+})$ IN AQUEOUS SOLUTIONS OF H_2SO_4

% H_2SO_4 by wt	$\varepsilon \frac{1}{\text{Mole cm}}$	$\lg \frac{C_B}{C_{BH^+}}$	H_0	pK_{BH^+}
0·00	$3{\cdot}36 . 10^3$	—	—	—
23·3	$2{\cdot}99 . 10^2$	−1·01	−1·34	−0·33
24·7	$2{\cdot}46 . 10^2$	−1·11	−1·44	−0·33
26·3	$1{\cdot}96 . 10^2$	−1·21	−1·55	−0·34
28·1	$1{\cdot}49 . 10^2$	−1·34	−1·68	−0·34
30·1	$1{\cdot}08 . 10^2$	−1·49	−1·83	−0·34
31·6	$7{\cdot}75 . 10^1$	−1·64	−1·94	−0·30
34·8	$4{\cdot}97 . 10^1$	−1·84	−2·16	−0·32
38·2	$2{\cdot}76 . 10^1$	−2·11	−2·41	−0·30
41·5	$1{\cdot}49 . 10^1$	−2·40	−2·65	−0·25
42·1	$1{\cdot}36 . 10^1$	−2·44	−2·70	−0·26
46·4	6·51	−2·83	−3·07	−0·24
46·7	6·23	−2·86	−3·10	−0·24
49·3	4·39	−3·08	−3·34	−0·26
51·1	3·32	−3·29	−3·52	−0·23
51·8	3·24	−3·31	−3·58	−0·27
54·0	2·60	−3·53	−3·80	−0·27
56·3	2·25	−3·71	−4·07	−0·36
58·6	1·92	−4·02	−4·34	−0·32
60·5	1·74	−4·38	−4·57	−0·21

Note: $\lg(C_B/C_{BH^+})$ were computed from the values of absorption coefficients for the non-ionized form $\varepsilon_B = 3{\cdot}36 . 10^3$(1/Mole cm) and ionized form $\varepsilon_{BH^+} = 1{\cdot}60$(1/Mole cm) at $\lambda = 410\ m\mu$.

TABLE 5. SOLUBILITY AND f_B VALUES OF ORTHONITROANILINE IN AQUEOUS SOLUTIONS OF H_2SO_4

% H_2SO_4 by wt	$S\,\frac{\text{Mole}}{\text{litre}}$	H_0	f_B
0·0	8·61 . 10^{-3}	—	1·00
4·5	1·36 . 10^{-2}	+0·04	0·90
9·2	2·27 . 10^{-2}	−0·37	0·79
14·2	3·05 . 10^{-2}	−0·75	1·02
19·2	6·09 . 10^{-2}	−1·09	0·96
20·1	6·55 . 10^{-2}	−1·10	0·91
24·8	1·21 . 10^{-1}	−1·46	1·03
25·0	1·09 . 10^{-1}	−1·47	1·17
29·8	2·52 . 10^{-1}	−1·81	1·07
32·1	3·44 . 10^{-1}	−1·97	1·12
35·6	6·96 . 10^{-1}	−2·24	1·02
35·9	8·37 . 10^{-1}	−2·26	0·89

TABLE 6. *o*-NITROANILINE f_B VALUES, AS MEASURED FROM THE COEFFICIENT OF DISTRIBUTION BETWEEN THE ACID AND CCl_4

% H_2SO_4 by wt.	24·5	29·9	35·0	40·2	46·3	49·3	54·9	60·0	62·6
f_B	1·01	0·934	0·761	0·621	0·427	0·298	0·250	0·287	0·525

DISCUSSION

In studying the ionization of *p*- and *o*-nitroanilines and diphenylamine in aqueous solutions of sulphuric acid, it was necessary to make clear whether the calculated value of pK_{BH^+} remains constant under conditions when practically the whole of the substance is present in the ionized form, BH^+. As shown by the data in Tables 1, 4 and 7, for these substances pK_{BH^+} remains constant for high C_{BH^+}/C_B values

Consequently, over a wide range of acidity:

$$\frac{f_A}{f_{AH^+}} = \frac{f_B}{f_{BH^+}} = \frac{f_C}{f_{CH^+}} = \cdots$$

The activity coefficients of the non-ionized form of these indicators within the investigated range of sulphuric acid concentrations vary in a different way. Then, in 30% H_2SO_4, f_B of *p*-nitroaniline was observed to increase 1·2 times as compared with water, f_B of diphenylamine increased 2·7 times; whereas for *o*-nitroaniline the f_B coefficient was practically constant in this range of acid concentrations. Boyd's data[1] also testify to the activity coefficients varying in a different way according to the concentration of the acid. This conclusion is likewise supported by the results of Hammett and Chapman's work,[6] in which the solubility of Π-benzoyldiphenyl in aqueous solutions of sulphuric acid was measured. Given in Table 9 are the solubility of Π-benzoyldiphenyl and the $[1 + (h_0/K_{BH^+})](1/S)$ values proportional to the activity coefficient of the non-ionized form.*

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* Note. The solubility of Π-benzoyldiphenyl in water is unknown; it is, therefore, impossible to obtain f_B for the usually adopted standard state.

[6] L. P. Hammett and R. P. Chapman, *J. Amer. Chem. Soc.* **56**, 1282 (1934).

TABLE 7. MOLAR ABSORPTION COEFFICIENT AND $\lg(C_B/C_{BH^+})$ OF DIPHENYLAMINE IN AQUEOUS SOLUTIONS OF H_2SO_4 AT $\lambda = 280\ m\mu$

% H_2SO_4 by wt	$\varepsilon \frac{1}{\text{Mole cm}}$	$\lg \frac{C_B}{C_{BH^+}}$	H_0	pK_{BH^+}
0·00	1·38 . 10^4	—	—	—
0·497	9·90 . 10^3	0·40	+1·16	+0·76
0·796	8·59 . 10^3	0·20	+0·97	+0·75
1·00	7·86 . 10^3	0·12	+0·86	+0·74
1·26	7·16 . 10^3	0·10	+0·77	+0·67
1·51	6·48 . 10^3	0·01	+0·70	+0·69
1·89	5·64 . 10^3	−0·16	+0·59	+0·75
2·54	4·53 . 10^3	−0·31	+0·42	+0·73
3·06	3·89 . 10^3	−0·41	+0·30	+0·71
3·72	3·24 . 10^3	−0·51	+0·16	+0·67
4·43	2·71 . 10^3	−0·61	+0·05	+0·66
5·25	2·28 . 10^3	−0·70	−0·05	+0·65
6·20	1·86 . 10^3	−0·81	−0·13	+0·68
7·38	1·50 . 10^3	−0·91	−0·23	+0·68
8·62	1·26 . 10^3	−1·00	−0·33	+0·67
9·76	9·82 . 10^2	−1·12	−0·41	+0·71
10·6	8·66 . 10^2	−1·17	−0·48	+0·71
11·1	7·63 . 10^2	−1·23	−0·52	+0·71
12·9	6·25 . 10^2	−1·32	−0·65	+0·67
14·4	4·81 . 10^2	−1·44	−0·77	+0·67
16·2	3·67 . 10^2	−1·56	−0·87	+0·69
18·2	2·70 . 10^2	−1·70	−0·99	+0·71
20·3	1·96 . 10^2	−1·84	−1·12	+0·72
22·1	1·45 . 10^2	−1·97	−1·26	+0·71
22·3	1·31 . 10^2	−2·02	−1·27	+0·75
23·4	1·19 . 10^2	−2·06	−1·35	+0·71
24·2	9·56 . 10^1	−2·16	−1·41	+0·75
26·0	6·78 . 10^1	−2·31	−1·54	+0·77
27·7	5·04 . 10^1	−2·44	−1·66	+0·78
29·2	3·90 . 10^1	−2·55	−1·76	+0·79
30·3	3·15 . 10^1	−2·64	−1·84	+0·80
30·9	2·81 . 10^1	−2·69	−1·88	+0·81

TABLE 8. SOLUBILITIES AND ACTIVITY COEFFICIENTS OF DIPHENYLAMINE NON-IONIZED FORM IN AQUEOUS SOLUTIONS OF H_2SO_4

% H_2SO_4 by wt	$S \frac{\text{Mole}}{\text{litre}}$	H_0	f_B
0·00	2·63 . 10^{-4}	—	1·00
5·00	1·28 . 10^{-3}	−0·02	1·31
10·0	2·6 . 10^{-3}	−0·43	1·50
13·0	3·55 . 10^{-3}	−0·66	1·81
17·1	5·99 . 10^{-3}	−0·92	1·92
20·0	7·75 . 10^{-3}	−1·10	2·22
25·4	2·01 . 10^{-2}	−1·50	2·13
29·8	3·30 . 10^{-2}	−1·81	2·65
30·6*	—	—	2·82

Note: Distribution experiments are marked by asterisks. The remaining f_B values have been obtained from the t solubility.

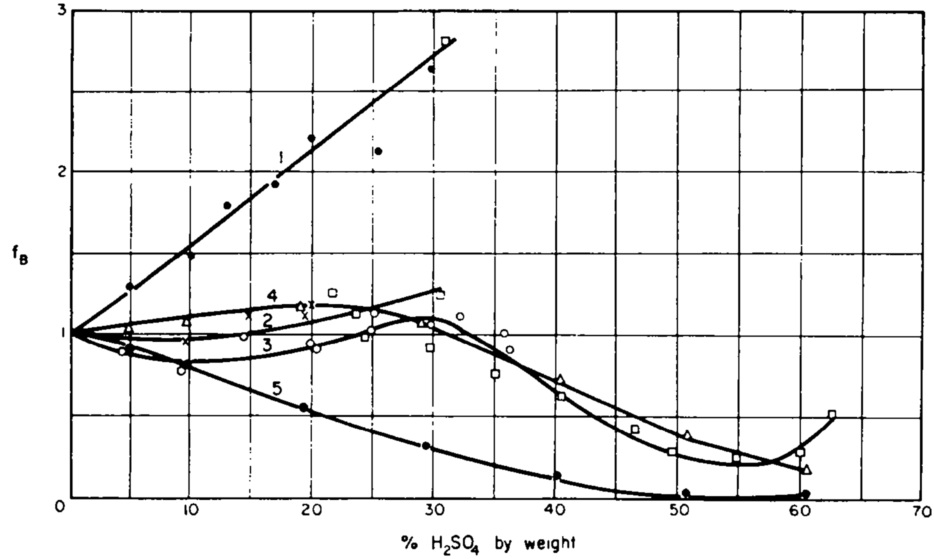

FIG. 1. f_B of Diphenylamine
FIG. 2. f_B of *p*-Nitroaniline
FIG. 3. f_B of *o*-Nitroaniline
FIGS. 4 and 5. f_B of 2,6-Dichloro-4-nitroaniline and 2,4,6-Trinitroaniline, according to Boyd.[3]

Note: squares denote experiments on the distribution coefficient. The other f_B values were obtained from solubility data.

TABLE 9

Π-Benzoyldiphenyl				2,4,6-Trinitroaniline		
% H_2SO_4 by wt	H_0	S $\frac{\text{Mole}}{\text{litre}}$	$\lg\left[\frac{1}{S}\left(1+\frac{h_0}{K_{BH^+}}\right)\right]$	% H_2SO_4 by wt	f_B	$\lg f_B$
70·34	−5·97	$2{\cdot}8 \,.\, 10^{-5}$	4·64	70·0	$1{\cdot}18 \,.\, 10^{-2}$	−1·93
75·35	−6·77	$3{\cdot}57 \,.\, 10^{-4}$	3·84			
77·40	−7·13	$1{\cdot}29 \,.\, 10^{-3}$	3·53			
78·70	−7·31	$2{\cdot}87 \,.\, 10^{-3}$	3·32	78·2	$6{\cdot}43 \,.\, 10^{-3}$	−2·19
79·77	−7·49	$1{\cdot}38 \,.\, 10^{-3}$	2·80			

Given in the above Table for comparison are the values for 2,4,6-trinitroaniline.[1]

How can such results be interpreted. In very diluted solutions of the acid, the activity coefficients of ions and molecules are assumed to be equal to unity and $f_B/f_{BH^+} = 1$. Apparently, in a general case the ratio f_B/f_{BH^+} must depend on the concentration of the acid.

Suppose that in an arbitrarily chosen concentrated aqueous solution of a strong acid "N" the ratio $f_B/f_{BH^+} = m$ and also suppose that as we pass from the very dilute solution to the "N" solution, the activity coefficient of the non-ionized form for the "A" substance has changed "a" times, for the "B" substance "b" times. and for the "C" substance "c" times. For the relations

$$\frac{f_A}{f_{AH^+}} = \frac{f_B}{f_{BH^+}} = \frac{f_C}{f_{CH^+}} = m$$

to remain valid, the equalities

$$f_{AH^+} = \frac{a}{m}\,; \quad f_{BH^+} = \frac{b}{m}\,; \quad f_{CH^+} = \frac{c}{m}$$

must be satisfied.

Consequently, the activity coefficients of the ionized form of AH^+, BH^+, CH^+ types vary 1/m times, as compared to the variation of the activity coefficient of the non-ionized form, the m value being independent of the ion structure. It could be supposed that the structure of the molecule or ion affects the value of "a", "b" and "c", whereas factor 1/m reflects the specificity of the protonated molecule. The Hammett relationship, however, is applicable to other types of ionization as well, particularly, to the process of proton addition to the once protonated molecule:

$$AH^+ + H^+ = AH_2^{2+}$$

Bonner and Lockart[7] have shown the addition of proton to the once protonated molecules of 4-nitro-1,2-phenylendiamine in the range from 30 to 55% H_2SO_4 by wt and of 4-aminoacetophene in the range from 75 to 95% H_2SO_4 by wt to be characterized by the acidity function h_0. Earlier Brandt *et al.*[8] have shown that proton addition to the ionized form of Π-nitroaniline to be likewise described by the H_0 function.

Consequently, in such processes

$$\frac{f_{BH^+}}{f_{BH_2^{2+}}} = \frac{f_B}{f_{BH^+}}\,;$$

If in the "N" solution $f_B/f_{BH^+} = m$, then $f_{BH^+}/f_{BH_2^{2+}} = m$. Suppose that, as we pass from a very dilute solution of the acid to the "N" solution, f_B has changed "b" times, then $f_{BH^{2+}}$ must have changed b/m^2 times. The h_0 function can also be used to describe the dissociation of strong organic acids in aqueous solutions of minerals acids:

$$AH \rightleftarrows A^- + H^+$$

e.g. the dissociation of picric acid in the aqueous solutions of sulphuric and perchloric acid.[9] The ratio of C_{A^-} to C_{AH} concentrations varies according to acidity "h_0". The dissociation constant remains invariable within a wide range of h_0, i.e. for such a process the equation

$$\frac{f_{A^-}}{f_{AH}} = \frac{f_B}{f_{BH^+}}$$

is satisfied. Apparently, in the "N" solution the activity coefficient of the f_{A^-} ion is equal to m . a, where "a" is the variation of the activity coefficient of the non-ionized form f_{AH}. Thus, it appears that if $m \neq 1$ the effect of the medium on the ion is characterized by two quantities: the variation of the activity coefficient of the non-ionized form "f_B" and the value of "m". For the anion $f_{A^-} = a \,.\, m$. For a single-charge positive ion $f_{AH^+} = a/m$ and for a double-charge positive ion $f_{AH^{2+}} = a/m^2$.

Hammett's hypothesis is applicable not only to ionization of organic molecules, but also to that of sulphuric acid. As is known,[10] for the solutions containing over

[7] T. G. Bonner and I. C. Lockhart, *J. Chem. Soc.* 364 (1957).

[8] J. C. D. Brand, W. C. Horning and M. B. Rhornley, *J. Chem. Soc.* 1374 (1952).

[9] R. H. Boyd, *J. Phys. Chem.* **67**, 737 (1963).

[10] J. C. D. Brand; *J. Chem. Soc.* 997 (1950), N. C. Deno and R. W. Taft, *J. Amer. Chem. Soc.* **76**, 245 (1954).

92% H_2SO_4 the following equation is valid:

$$\lg \frac{m_{H_2SO_4}}{m_{HSO_4^-}} = H_0 = \text{const, i.e.} \frac{f_{H_2SO_4}}{f_{HSO_4^-}} \cdot \frac{f_B}{f_{BH^+}} = \text{const.}$$

In such solutions the activity of the non-dissociated sulphuric acid is proportional to its molar fraction.[11] Consequently, the coefficient $f_{H_2SO_4}$ is invariable, if the concentration of the non-dissociated acid is expressed in molar fractions. If for any solution $f_B/f_{BH^+} = m$, then $f_{HSO_4^-}/f_{H_2SO_4}$ is also equal to m.

In other words, when the ionized particle is transferred from a very dilute solution of an acid to a concentrated aqueous solution of a strong acid, the variation of the free energy of the ionized particle can be represented as composed of two parts: one corresponding to the variation of the specific energy of a neutral particle of a similar structure, F_1, and the other, F_2, determined by the charge alone, being independent of the ion structure. The substances investigated, for which Hammett's hypothesis holds, contain functional groups, such as amino, nitro and carbonyl groups, etc. On the above evidence it can be expected that the addition of proton to different functional groups will have a similar effect on the value of the activity coefficient of the ionized molecule. However, in substances with such functional groups the solubility is observed to vary considerably according to the strength of the acid. Thus, we may suppose that these groups are mainly responsible for the variation of the activity coefficient of the non-ionized molecules. The addition of a charge will undoubtedly affect the properties of the molecule as a whole and, particularly, of the atoms in the functional group which has obtained the charge. The contribution of the charge to the free energy of the ionized molecule being great, the properties of all the atoms in the molecule and, particularly, of those in the charged functional group will be substantially changed. In that case the variation of the free energy is not to be conceived as a sum of two independent addends, as must be the case if f_B/f_{BH^+} depends on the solvent composition. If, on the other hand, the effect of the charge is insignificant, the free energy of the ion can be represented as the sum of $F_1 + F_2$ and the F_2 contribution can be neglected. In solutions with a high concentration of electrolyte the non-ionized and ionized molecules are within reach of the solvate shell ions. The possibility that the effect of the solvate shell ions on the non-ionized molecule is equivalent to the ionized molecule charge is by no means ruled out. The exchange interaction apparently accounts for the main contribution to the free energy of the ions and non-ionized particles. If so, the difference in the free energy variation between the ionized and non-ionized particles must vanish. In that case the value of f_B/f_{BH^+} must be independent of the strength of the acid and to be equal to unity, as adopted for a dilute solution. In very dilute aqueous solutions of the acid, for which the Debye-Huckel equation is valid, the electrostatic interaction is most pronounced. The activity coefficients f_B in such mediums are, as a rule, constant, and the contribution of electrostatic interaction to the activity coefficients f_{H^+} and f_{BH^+} becomes smaller. In more concentrated solutions, the acidity function describes the variation of the hydrogen ion activity $h_0 = a_{H^+}$.

The fact that the acidity function is equal to the minus logarithm of proton activity does not mean that the ionization of organic molecules in acid medium must be described by the h_0 function alone. This function cannot be applied unless the

[11] B. Gutbezahl and E. Grunwald, *J. Amer. Chem. Soc.* **75**, 559 (1953).

Hammett relationship is satisfied. The ionization of organic molecules, however, may involve not only the addition of the proton.*

In acid medium, the ion pairs are also likely to appear by addition of the acid molecule to the B molecule.

The data cited by Arnett and Mach[12] can sometimes be applied if it is assumed that, apart from the formation of ions, ion pairs of the type

$$BH^+ . HSO_4^-$$

are formed. In some cases the ion and the non-ionized form may differ in structure; then there is a possibility of the ratios of the activity coefficients of the two forms losing constancy. In our view, this occurs in the ionization of cyancarbonic acids.[9]

The independence of f_B/f_{BH^+} on concentration of the aqueous solution of strong acid was suggested in 1953 by Gutbezhal and Grunwald.[11]

Rybkin and Shevchenko have reported recently that the activity of protons in aqueous solutions of hydrochloric acid measured by using an electrochemical technique is proportional to the medium acidity h_0, as measured by the indicator method.[14]

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* In the given case we have in mind the ionization of the arylcarbinol type.

[12] E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.* **86**, 2671 (1964).

[13] R. S. Ryabova, I. M. Medvetskaya and M. I. Vinnik, *Zh. Fiz. Khim.* **40**, 339 (1966).

[14] Yu. F. Rybkin and N. F. Shevchenko, *Elektrokhimiya* **1**, 1, 46 (1965).