[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

The Application of Activity Coefficient Data to the Relations between Kinetics and Acidity Functions[1]

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Equations are developed relating kinetic rate constants to acidity functions in aqueous solutions of strong acids. To use these equations it is necessary to know the general behavior of activity coefficients of cations and neutral molecules in these media. For this purpose activity coefficients of three salts and fourteen neutral molecules have been measured as a function of sulfuric acid concentration. The method of applying these values is outlined.

The Hammett H_0 function,[2] defined by eq. 1, has been successful in describing shifts in equilibria of the type $B + H^+ = BH^+$ which are brought about by variation of the ratio of a strong acid to a polar liquid such as water or acetic acid. This success is dependent on H_0 being a function only of acid concentration and not of other variables such as the structure of the base B.

$$H_0 = (pK_{BH^+}) + \log (c_B/c_{BH^+}) = -(\log a_{H^+}) - \log (f_B/f_{BH^+}) \quad (1)$$

A similar situation prevails in the case of the C_0 function,[3] which is defined by eq. 2.

$$C_0 = (pK_{R^+}) + \log (c_{ROH}/c_{R^+}) = -(\log a_{H^+}) + \log a_{H_2O} - \log (f_{ROH}/f_{R^+}) \quad (2)$$

For reactions in which the transition state is composed of the reactants H^+, A_1, A_2, . . ., eq. 3 is the Brönsted form of the rate equation. The terms in the brackets will be constants at a particular concentration of sulfuric acid and will correspond to the experimental rate constant, k_{exp}. The logarithm of the expression for k_{exp} can be combined with eq. 1 to give eq. 4 after differentiation with respect to % H_2SO_4. The symbol B represents the indicators used to evaluate the H_0 acidity function.[2]

$$\mathrm{d}c_A/\mathrm{d}t = c_{A_1}c_{A_2}\ldots[k(f_{A_1}f_{A_2}\ldots/f^*)a_{H^+}] \quad (3)$$

$$\mathrm{d} \log k_{exp}/\mathrm{d}\ \%H_2SO_4 = -\mathrm{d}\ H_0/\mathrm{d}\ \%H_2SO_4 + \mathrm{d} \log (f_{A1}f_{A2}\ldots f_{BH^+}/f_Bf^*)/\mathrm{d}\ \%\ H_2SO_4 \quad (4)$$

In a similar way, eq. 5 can be derived for reactions of the type of eq. 6. The symbol ROH represents the alcohols used to evaluate the C_0 acidity function.[3]

$$\mathrm{d} \log k_{exp}/\mathrm{d}\ \%\ H_2SO_4 = -\mathrm{d}C_0/\mathrm{d}\ \%\ H_2SO_4 + \mathrm{d} \log (f_{A1}f_{A2}\ldots f_{SOH}f_{R^+}/f_{ROH}f^*)/\mathrm{d}\ \%\ H_2SO_4 \quad (5)$$

$$SOH + H^+ = H_2O + S^+ \xrightarrow[\text{rate-determining}]{+\ A_1,\ A_2,\ \ldots} \text{products} \quad (6)$$

Values of $-\mathrm{d}H_0/\mathrm{d}$ % H_2SO_4 and $-\mathrm{d}C_0/\mathrm{d}$ % H_2SO_4 are known for several water–strong acid media so that the principal barrier to applying eq. 4 and 5 is in the estimation of the last term in each equation. The development of methods of estimating these terms will be the concern of this paper.

Experimental

The activity coefficients of most of the compounds were determined by measuring the solubility of the compound in different concentrations of sulfuric acid at 25 ± 0.1°. The pure substance was chosen as the standard state unless otherwise noted so that the activity coefficients were simply the reciprocal of the concentration of the saturated solutions. Since the solubilities were of the order of 10^{-2} molar or less, the value of the activity coefficient is probably a function only of the sulfuric acid concentration and in particular is not a function of the concentration of solute. The log of the activity coefficients were plotted against % H_2SO_4 and the slopes visually estimated to obtain values of d log f/d % H_2SO_4.

The substances studied were both solids and liquids. An excess of solute was shaken vigorously with the appropriate concentration of sulfuric acid in a water-bath thermostated at 25 ± 0.1°. The concentration of the solution was periodically measured until a constant value was reached. This required several minutes for the liquids and several hours for the solids. The saturated solutions were removed from excess solute by carefully removing an aliquot with a pipet. Centrifugation was necessary with some of the liquids and the tetraphenylphosphonium and tetrabutylammonium[4] perchlorate solutions required filtration.

The concentrations of potassium perchlorate and tetrabutylammonium perchlorate were determined by analyzing for perchlorate ion using the excellent procedure of Willard and Perkins.[5] This involved treating a known volume of the saturated solution with a sodium chloride solution and then with a dilute aqueous solution of tetraphenylphosphonium chloride. The precipitated tetraphenylphosphonium perchlorate was filtered, washed, dried at 110° and weighed. The method was found to be unaffected by variations in the sulfuric acid concentration from 0 to 10%.

The concentrations of tetraphenylphosphonium perchlorate in the different sulfuric acid solutions were determined spectroscopically using measurements at 268 and 276 mμ. Above 80% sulfuric acid the salt was unstable so that the data at 80% acid are of doubtful accuracy. Measurements were made on the tetraphenylphosphonium perchlorate solutions to show that there was no significant variation in the extinction coefficients between 0 and 60% sulfuric acid.

The concentrations of the remaining compounds were determined spectroscopically. No correction was made for variation of extinction coefficient with sulfuric acid concentration. In two cases, chlorobenzene and methoxybenzene, this variation was studied and found to be less than 5% over the range of acid concentrations studied for each of these two compounds.

The activity coefficients for acrylonitrile were determined from distribution experiments between an alkane fraction that was primarily pentane and the appropriate sulfuric acid solution. The pentane was purified by shaking with sulfuric acid until the absorption at 225 mμ was negligible. The concentration of acrylonitrile in the pentane was determined spectroscopically using data at 225 mμ. The concentration of acrylonitrile in the sulfuric acid solution was computed by difference. The solution of acrylonitrile in pentane was assumed to exhibit ideal behavior for the dilute ranges studied and the standard state was chosen so that activity equaled the molar concentration of acrylonitrile in pentane. The activity coefficients were thus the concentra-

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[1] Grateful acknowledgment is made of the support of this research by a grant from the Petroleum Research Fund of the American Chemical Society.

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, Chapter IX.

[3] N. Deno, J. Jaruzelski and A. Schriesheim, THIS JOURNAL, **77**, 3044 (1955).

[4] Dr. R. P. Seward kindly supplied a sample of this salt.

[5] H. Willard and L. Perkins, *Anal. Chem.*, **25**, 1634 (1953).

TABLE I

SOLUBILITIES AND ACTIVITY COEFFICIENTS OF SALTS AS A FUNCTION OF % H_2SO_4

% H_2SO_4	Solubility (moles/l.) I[c]	II[c] $(\times 10^4)$	III[c]	Log $f\pm$[a,b] I	II	III	d log $f\pm$/d % H_2SO_4[b] I	II	III
0.0	0.1470	3.42	0.01023	0.832	3.467	1.990	−0.016	−0.018	−0.018
5.06	.1675	4.06	.01189	.766	3.390	1.925	− .001	− .006	− .006
12.40	.1605	4.00	.01100	.795	3.398	1.958	+ .007	+ .007	+ .007
20.35	.1360	3.62	.01033	.866	3.440	1.986	+ .012	− .002	.0
30.6	.1020	4.05	.01136	.991	3.392	1.945	+ .012	− .009	− .010
40.4	.0782	5.76	.01638	1.107	3.239	1.786	+ .009	− .023	− .020
50.4	.0677	10.48	.02945	1.172	2.979	1.531	+ .004	− .030	− .030
60.2	.0668	24.0	.06325	1.176	2.62	1.199	.0	− .043	− .042
70.0	.0661	72.0	.1993	1.180	2.14	(0.700)[d]	.0	− .041	− .05
80.5	.0680	164.0	.3014	1.168	1.78	(0.521)[d]	− .003	− .027	
90.5	.0965			1.016			− .040		
96.7	.1785			0.748			−.040		

[a] The activity of the solid at 25° was defined as unity so that the mean activity coefficient ($f\pm$) was the reciprocal of the concentration of the saturated solution. [b] If it is assumed that $f_{K^+} = f_{ClO_4^-}$, the values under I are also those for K^+ and ClO_4^-, the values under II are those for the tetraphenylphosphonium ion and the values under III are those for the tetrabutylammonium ion. [c] I is potassium perchlorate; II is tetraphenylphosphonium perchlorate; III is tetrabutylammonium perchlorate. [d] These values are inaccurate because the phase in equilibrium with the saturated solution was a liquid rich in III and not solid III. Solid III was regenerated from this liquid phase on dilution with water.

tion in pentane divided by the concentration of acrylonitrile in the aqueous sulfuric acid layer.

Table I summarizes the data on the solubilities of the three salts studied. A method for estimating d log f/d % H_2SO_4 for several single ions is given in footnote (*b*) in Table I. Table II lists values of d log (f_1/f_2)/d % H_2SO_4 for three pairs of cations as well as values for the single ion ROH_2^+. Table III summarizes the data on the solubilities of neutral species. Table IV summarizes the distribution data on acrylonitrile. Table V lists values of d log f/d % H_2SO_4 for the neutral species studied as well as some computed from the solubility data of Hammett and Chapman.[6]

TABLE II

VALUES OF d LOG (f_1/f_2)/d %H_2SO_4 FOR PAIRS OF CATIONS

%H_2SO_4	d log (f_1/f_2)/d %H_2SO_4[a] $\frac{f_{K^+}}{f_{(C_6H_5)_4P^+}}$	$\frac{f_{K^+}}{f_{(C_4H_9)_4N^+}}$	$\frac{f_{(C_6H_5)_4P^+}}{f_{(C_4H_9)_4N^+}}$	$\frac{f_{ROH_2^+}}{f_{R^+}}$[b]
0.0	0.004	0.004	0.000	
5.06	.010	.010	.000	0.055
12.40	.000	.000	.000	.042
20.35	.028	.024	− .004	.050
30.6	.042	.044	+ .002	.067
40.4	.064	.058	− .006	.065
50.4	.068	.068	.000	.068
60.2	.086	.084	− .002	.095
70.0	.082	.10	+ .02	.063
80.5	.048			.00

[a] The only assumption required to compute these values was that the activity coefficients of the ions were independent variables. [b] Ref. 3.

Discussion

Activity Coefficients of Molecules.—For the neutral molecules, the data in Table V demonstrate that d log f/d %H_2SO_4 was remarkably independent of structure from 0–60% sulfuric acid. This result was obtained despite considerable variation in size and functional groups of the neutral molecules. Also the values of this function were small, generally varying between +0.02 and −0.02. This is in agreement with the small Setschenow parameters[7] that have been found for aqueous solutions of strong acids. From 60–90% sulfuric acid, d log f/d %H_2SO_4 for benzene and chlorobenzene remain in the range 0 to −0.03 and this result probably prevails for other non-polar solutes.

TABLE III

SOLUBILITIES OF ORGANIC COMPOUNDS AS A FUNCTION OF % H_2SO_4

% H_2SO_4	Solubility[a] C_6H_6 264	$(C_6H_6)_2$-CH_2 220	C_6H_5Cl 263.5	C_6H_6-OCH_3 286	C_6H_5-CH_2CH_2-OH 276	$(C_6H_6)_2$-CHOH (*c*)	$(C_6$-$H_6)_3$-COH (*c*)
0.0	0.775	0.990	0.790	0.415	0.498	2.80	5.5
5.06	.646	.720	.691	.345	.407	2.12	5.0
12.40	.532	.520	.549	.245	.362	1.57	4.5
20.35	.432	.395	.428	.189	.358	1.12	4.8
30.6	.363	.326	.384	.176		0.87	5.0
40.4	.334	.357	.393	.168		0.90	7.0
50.5	.332	.405	.400	.198		1.24	
60.2	.334	.495	.400				
70.0	.352	.590	.490				
80.5	.410		.665				
90.5			1.2[b]				

[a] The values listed in each column except the last two are the optical densities of the saturated solutions at the wave length (mμ) indicated under the formula of each compound. The wave length used was an absorption maximum with all but diphenylmethane and methoxybenzene. The concentration in moles/liter could be determined by measuring the extinction coefficient at the appropriate wave length and dividing it into the optical density listed in the table. [b] A value of 0.910 was obtained at 85% H_2SO_4. [c] The values in these two columns are the actual molarity of the alcohol multiplied by 10^3 for diphenylmethanol and by 10^6 for triphenylmethanol. The saturated solutions were diluted with 97% sulfuric acid and the concentrations of the resulting carbonium ions were measured spectroscopically. For diphenylmethanol, the data were measured at 442 mμ and an extinction coefficient of $10^{4.64}$ was used in the calculations. The corresponding values for triphenylmethanol were 431 mμ and $10^{4.60}$.

The substituted carboxylic acids studied by Hammett and Chapman[6] present an unusual situation in 60–90% sulfuric acids. Values of d log f/d %H_2SO_4 range from −0.03 to −0.14 (Table V). This unusual result was discussed by H. and C., who presented spectroscopic and cryoscopic evidence to show that the sharp increases in solubilities were not due to protonation of the carboxyl group.

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(6) L. P. Hammett and R. Chapman, THIS JOURNAL, **56**, 1282 (1934).

(7) F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

TABLE IV

VALUES FOR THE ACTIVITY COEFFICIENTS OF ACRYLONITRILE FROM DISTRIBUTION EXPERIMENTS

% H_2SO_4	Molarity of $CH_2{=}CH{-}CN$[a] I[b] Pentane layer	I[b] Aqueous layer	II[b] Pentane layer	II[b] Aqueous layer	Activity coefficient[c] in aqueous layer I	II
0.0	0.122	0.049	0.224	0.108	0.40	0.48
5.06	.118	.053	.218	.114	.44	.52
12.40	.114	.056	.208	.125	.49	.60
21.5	.109	.062	.197	.135	.57	.68
27.6	.104	.067	.193	.139	.64	.72
38.7	.110	.061	.200	.146	.55	.66
55.5	.127	.044	.240	.092	.34	.38
60.3	.130	.041	.256	.077	.31	.30

[a] The concentration in the pentane layer was determined spectroscopically using data at 225 mμ. The extinction coefficient for acrylonitrile at 225 mμ was 1.58. The concentration in the aqueous layer was determined by the difference between the initial and equilibrium concentrations of the acrylonitrile in pentane. [b] The initial concentration of acrylonitrile in series II was about twice that in series I. This had an appreciable effect on the activity coefficients as shown in the last two columns. The data in column I are an average of 2 or 3 runs in which the maximum deviation from the average was 5%. The data in column II were more erratic. The maximum deviation from an average of three runs ranged from 5–12%. The values of d log f_{RCN}/d % H_2SO_4 which appear in Table V are based on the data in column I. [c] The activity coefficients were the concentrations in the aqueous layers divided by the concentrations in the pentane layers.

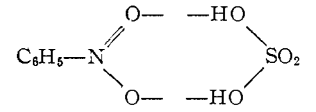
TABLE V

VALUES OF d LOG f/d %H_2SO_4 FOR NEUTRAL MOLECULES AT 25°

% H_2SO_4 =	0	5	10	20	30	40	50	60	70	75	80	85	90
							d log f/d % H_2SO_4						
Benzene	0.02	0.02	0.01	0.01	0	0	0	0	0	−0.01	−0.02		
Diphenylmethane	.03	.03	.02	.01	0	0	−0.01	−0.01	−0.01				
Chlorobenzene	.02	.02	.01	.01	0	0	0	0	− .01	− .02	− .02	−0.03	−0.02
Methoxybenzene	.02	.02	.02	.01	0	0	−0.01						
2-Phenylethanol	.02	.01	0	0									
Diphenylmethanol	.02	.02	0.02	0.01	0	−0.01	−0.02						
Triphenylmethanol	.01	.01	0	0	−0.01	− .03							
Acrylonitrile	.007	.007	.007	.007	0	− .012	− .012	−0.012					
2-Methyl-2-butene[a]	.01	.01	.01										
Nitrobenzene[b]	.01	.01	.01	0	0	− .02	− .02	− .03	− .03	− .03	− .03		
Benzoic acid[b]	.02	.02	.02	.02	0.01	0	0	− .01	− .05	− .07			
Phenylacetic acid[b]	.01	.01	.02	.02	.01	0	−0.01	− .02	− .04	− .10			
2-Nitrobenzoic acid[b]	.03	.03	.02	.02	.01	0	0	− .01	− .03	− .05	− .07	− .11	
4-Nitrobenzoic acid[b]	.01	.01	.01	.01	.01	0	−0.01	− .02	− .05	− .05	− .08	− .14	

[a] Computed from the data of R. W. Taft, Jr., E. Purlee and P. Riesz, which were measured at 30° (THIS JOURNAL, **77**, 899 (1955)). [b] Computed from the data of Hammett and Chapman (ref. 6).

A similar situation exists for nitrobenzene. The data of Hammett and Chapman[6] do not extend beyond 80% sulfuric acid. However, semi-quantitative experiments showed that nitrobenzene exhibits a very sharp increase in solubility from 80–97% acid. The solubilities expressed in % nitrobenzene were < 1% in 85% acid, 29% in 90.5% acid, 50% in 93.8% acid and 89% in 96.7% acid. Thus nitrobenzene and 96.7% acid were miscible from 0–89% nitrobenzene. These large solubilities cannot be due to protonation since spectroscopic and cryoscopic data showed that nitrobenzene is less than 1% protonated in 97% acid.[8] It is entirely possible that these sharp changes in solubilities are due to as yet unknown equilibria. For example nitrobenzene might form a stable C_6H_5-$NO_2 \cdot H_2SO_4$ species represented by structure I. The qualitative solubility data support such a hypothesis.



I

In summary, the nitro compounds and carboxylic acids, which contain two oxygen atoms in 1,3-relation, have appreciable values of d log f/d $\leqq H_2SO_4$ from 60–100% sulfuric acid and it is advisable to estimate the value of the last term in either eq. 4 or 5 when such species are involved.

Activity Coefficients of Ions.—The ionic activity coefficients in eq. 4 and 5 appear as the ratio of the activity coefficients of two cations. Although it is generally not possible to evaluate activity coefficients of single ions without rather tenuous assumptions, the ratio of the activity coefficients of two cations can be determined with no assumption other than that the activity coefficients of cation and anion are independent variables. The values of four such ratios appear in Table II for a range of concentrations of sulfuric acid.

It was anticipated that these cation activity coefficient ratios would have a limited set of values for certain characteristic types of cation structures. Support for this concept is already apparent in Table II as evidenced by identical values for d log $(f_{K^+}/f_{(C_6H_5)_4P^+})$/d %$H_2SO_4$ and d log $(f_{K^+}/f_{(C_4H_9)_4N^+})$ at all acid concentrations studied. Bartlett and Arnett[9] suggested that the categories may depend on the effective electrical field that acts on the solvent. Thus ions in which the charges are well shielded from the solvent such as the tetraphenylphosphonium ion and tetrabutylammonium ion will fall into a single category. Small unshielded ions and perhaps ions containing an unshielded charge on the periphery of an organic moiety would comprise two other categories.

As data become available it will be possible to estimate d log (f_{cation}/f^*)/d %H_2SO_4 values in eq. 4 and 5 by choosing values for ions structurally similar to the cation and transition state under investigation.

Nature of the Transition State.—Equations 4 and 5 are not only useful in identifying the composition

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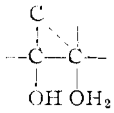
[8] J. C. D. Brand, *J. Chem. Soc.*, 997 (1950); L. P. Hammett, *J. Chem. Phys.*, **8**, 644 (1940); R. J. Gillespie and D. J. Millen, *Quart. Revs.*, **2**, 292 (1948).

[9] Contributed in discussions.

of the transition state, but in favorable cases they can yield information regarding the type of bonding in the transition state. The method can most easily be explained by reference to the particular case of the pinacol rearrangement.

Two extreme structures can be envisioned for the transition state. In I, the rearrangement is a concerted process in which there is very little lengthening of the C–O bond in the transition state. In III, the carbonium ion forms in a rapid reversible equilibrium followed by a rate-determining rearrangement of the carbonium ion. With I, the kinetics would fit eq. 4 and the last term, which would contain $(f_{\text{glycol}} f_{BH^+}/f_B f^*)$, would be negligible. The values of d log f/d %H_2SO_4 for glycol and B would cancel (in 0–60% H_2SO_4) and the transition state is so like a protonated base that its term would cancel that of BH^+.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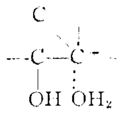
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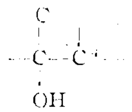
III

By an analogous argument, with III the kinetics would fit eq. 5 with a negligible last term.

In the case of II, eq. 4 would be applicable but the last term would become important. As the transition state became more and more like a carbonium ion, d log (f_{BH^+}/f^*)/d %H_2SO_4 would become appreciable and approach the value of d log $(f_{ROH_2^+}/f_{R^+})$/d %H_2SO_4 at extreme stretching of the C–O bond. In 0–50% sulfuric acid where d log a_{H_2O}/d %H_2SO_4 is small, d log $(f_{ROH_2^+}/f_{R^+})$/d %H_2SO_4 is just the difference between $-\mathrm{d}C_0$/d %H_2SO_4 and $-\mathrm{d}H_0$/d %H_2SO_4. The result is that as the transition state varies from I through II to III in a series of glycols, d log k/d %H_2SO_4 can be expected to change continuously from values equal to $-\mathrm{dH}_0$/d %H_2SO_4 to values equal to $-\mathrm{d}C_0$/d %H_2SO_4.

Hammett–Zucker Hypothesis.[2,10]—For reactions in which the transition state has the composition $(A \cdot H_2O \cdot H^+)$, eq. 7 can be derived from the Brönsted rate equation. Hammett and Zucker[10] found that the last term in eq. 7 appeared to be negligible for several reactions believed to be of this type. This result has been widely used[11] as a means of determining the composition of the transition state and in particular to decide whether water was or was not present.

$$\mathrm{d}\log k/\mathrm{d}\ \%H_2SO_4 = \mathrm{d}\log c_{H_3O^+}/\mathrm{d}\ \%H_2SO_4 + \mathrm{d}\log (f_A f_{H_3O^+}/f^*)/\mathrm{d}\ \%H_2SO_4 \quad (7)$$

It is our interpretation that the values of the last term in eq. 7 are more a function of the structural type of the ionic transition state than of its composition. Thus it is somewhat coincidental that most transition states containing a water molecule have the charge of the ion unshielded from solvent so that d log f/d %H_2SO_4 for H_3O^+ and the transition state approximately cancel (f_A usually makes a minor contribution). However, cases can be envisioned in which the charge is well embedded in the transition state and the last term in eq. 7 will become important despite the presence of water in the transition state. In such cases the value of d log $(f_{H_3O^+}/f^*)$/d %H_2SO_4 will approach d log $(f_{K^+}/f_{(C_6H_5)_4P^+})$/d %$H_2SO_4$ and thus the value of d log k/d %H_2SO_4 can approximate that of $-\mathrm{d}H_0$/d %H_2SO_4.

Acidity Functions.—For the bases used to evaluate H_0, calculations based on the data of Hammett and co-workers[12] showed that d log (f_{BH^+}/f_B)/d %H_2SO_4 did not vary generally by more than 0.01 unit at any particular concentration of sulfuric acid. The data in Table V show that d log f/d %H_2SO_4 for neutral species does not generally vary more than 0.02 unit from 0–60% acid. We can thus conclude that d log f_{BH^+}/d %H_2SO_4 also does not generally vary with structure by more than 0.02 unit in this region. This conclusion applies only to the BH^+ structures used to evaluate H_0. Thus in the 0–60% acid region the success of the H_0 and C_0 acidity functions is at least in part due to the invariance with structure of d log f/d %H_2SO_4 terms for B and BH^+ independently and for ROH and R^+ in the case of C_0. It is an open question whether a more precise invariance arises from the ratio f_{BH^+}/f_B than for f_{BH^+} and f_B separately.

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[10] L. Zucker and L. P. Hammett, THIS JOURNAL, **61**, 2791 (1939).

[11] F. A. Long, *et al.*, *ibid.*, **72**, 2367, 3692 (1950); **78**, 3326 (1956); *J. Phys. Colloid Chem.*, **55**, 829 (1951); R. W. Taft, Jr., THIS JOURNAL, **74**, 5372 (1952); R. P. Bell, A. L. Dowding and H. A. Noble, *J. Chem. Soc.*, 3106 (1955).

[12] L. P. Hammett and A. Deyrup, THIS JOURNAL, **54**, 2721 (1932); L. P. Hammett and M. Paul, *ibid.*, **56**, 827 (1934).