

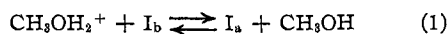
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA AND THE DEPARTMENT OF CHEMISTRY OF SOUTH DAKOTA STATE COLLEGE]

Acid-Base Indicators in Methanol. III. Concentration Ionization Constants of Indicators and Acids in Methanol

BY I. M. KOLTHOFF AND L. S. GUSS

In a previous communication,¹ thermodynamic ionization constants of a number of indicators and acids were determined in methanol by measuring $K = K_{I(c)}/K_{A(c)}$ at various ionic strengths and extrapolating to infinite dilution. Here, K , $K_{I(c)}$, and $K_{A(c)}$ are the conventional "concentration constants" and are dependent on the ionic strengths. The individual values of the constants $K_{I(c)}$ and $K_{A(c)}$ can be calculated from the measured values of K , if we have some means of evaluating one of them.

If a strong acid, as hydrochloric acid, is dissolved in methanol, there is practically a complete transfer of protons from the acid to the solvent.² If, to this solution, a small concentration of an appropriate indicator is added, the equilibrium



is established, which gives the constant

$$K_{I(c)} = \frac{c_{\text{CH}_3\text{OH}_2^+} c_{\text{I}_b}}{c_{\text{I}_a}} \quad (2)$$

Having this "concentration constant," we can determine the concentration ionization constant of any acid, defined by

$$K_{A(c)} = \frac{c_{\text{CH}_3\text{OH}_2^+} c_{\text{B}}}{c_{\text{A}}} \quad (3)$$

from the indicator equilibrium in an appropriate buffer solution of the acid, as

$$pK_{A(c)} = pK_{I(c)} - pK \quad (4)$$

where $pK = -\log K$. Buffer solutions of the same acid, in turn, can be used to evaluate concentration constants of other indicators, and so on.

In the present work, the "concentration constants" of tropeoline 00, methyl yellow, methyl orange and thymolbenzein have been determined in hydrochloric acid solutions in anhydrous methanol at varying ionic strengths. The methyl-oxonium ion concentration in the solutions is equal to the known concentration of the acid minus the concentration of the acid form of the indicator, which was determined experimentally. From the known concentration constants of methyl yellow and methyl orange and the equilibrium constant of

these indicators in trichloroacetate buffer,¹ the concentration ionization constant of this acid was calculated. In order to find the concentration constant of brom phenol blue, the concentration ionization constant of saccharin was determined in buffers of this acid and methyl orange. The equilibrium constant of the saccharin-brom phenol blue system was measured, leading to the concentration constant of this indicator. Moreover, the equilibrium constant of brom phenol blue has been determined in benzoate buffers and that of brom cresol purple in veronalate buffers.

Experimental

Materials.—The methods of purification of reagents have been discussed already.¹ The methanol used in making up solutions of hydrogen chloride contained less than 0.02% of water. Saccharin was precipitated from an aqueous solution of the sodium salt by hydrochloric acid. It was washed thoroughly with water, then recrystallized from acetone. Solutions of hydrogen chloride were prepared by passing hydrogen chloride gas through concentrated sulfuric acid, a plug of glass wool and finally through a wash bottle of methanol. The stock solution was standardized against standard sodium hydroxide solution.

Indicator-Buffer Systems.—Values of $pK = pK_{I(c)} - pK_{A(c)}$ were obtained by the method described in the previous paper.¹ A summary of rounded values is given in Table I.

Indicator-Hydrogen Chloride Systems.—To solutions of the desired concentration of hydrogen chloride were added solutions of known concentration of the indicator to be investigated. Comparison with standards was made by the method of Gillespie. As an example, in Table II are listed the data of thermodynamic constants obtained in a study of dimethylaminoazobenzene (methyl yellow). (Indicator concentration in the final solution = $2 \times 10^{-5} M$). The values of $pK_{I(c)}$ found in hydrochloric acid at small ionic strengths were corrected for the effect of the activity coefficient using the limiting Debye-Hückel expression.

(1) I. M. Kolthoff and L. S. Guss, *THIS JOURNAL*, **60**, 2518 (1938).

(2) D. M. Murray-Rust and H. Hartley, *Proc. Roy. Soc. (London)*, **A126**, 84 (1929).

TABLE I
VALUES OF pK OF INDICATOR-BUFFER SYSTEMS

Indicator	Acid	Ionic strengths									
		0.0	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.5
Methyl orange	Saccharin	-2.3	-2.3	-2.3	-2.3	-2.3 ^a	-2.2 ^a	-2.1 ^a	-2.0 ^a	-1.9 ^a	-1.8 ^a
Brom phenol blue	Saccharin	2.8	2.65	2.6	2.5	2.45	2.35	2.25 ^a	2.2 ^a	2.2 ^a	2.2 ^a
Brom phenol blue	Benzoic	-0.6	-0.75	-0.8	-0.85	-0.9 ^a	-1.0 ^a	-1.1 ^a	-1.1 ^a	-1.1 ^a	-1.1 ^a
Brom cresol purple	Benzoic	-1.45	-1.6	-1.7 ^a	-1.7 ^a	-1.8 ^a	-1.85 ^a	-1.85 ^a	-1.9 ^a	-1.9 ^a	-1.9 ^a

^a In the presence of LiCl.

TABLE II
DISSOCIATION OF METHYL YELLOW IN HYDROGEN CHLORIDE

$c_{H^+} \times 10^4$	$c_{Ib} : c_{Ia}$	pK_I
2.76	2.22	3.22
4.13	1.22	3.30
5.5	1.04	3.25
6.9	0.82	3.25
8.3	.63	3.28
9.7	.59	3.30
11.0	.45	3.30
12.4	.47	3.23
13.8	.40	3.25

Average 3.25

A summary of the results obtained is given in Table III. For comparison, values of the thermodynamic constants obtained in a previous study¹ in buffer solutions are included in the table. The latter values were based upon Goldschmidt's conductivity measurements.

TABLE III
DISSOCIATION CONSTANTS OF INDICATORS IN HYDROGEN CHLORIDE

Indicator	pK_I	
	In HC	Previous value
Tropeoline 00	2.2	...
Methyl yellow	3.25	3.4
Thymolbenzein	3.5	3.5
Methyl orange	3.85	3.8

In order to evaluate $pK_{I(c)}$ at higher ionic strengths, the indicator equilibrium of the above indicators was determined in solutions containing the same concentration of hydrochloric acid but varying concentration of lithium chloride. In Fig. 1, the values of $pr - pr_0$ are plotted against the square root of the ionic strength, where

$$pr = -\log \frac{c_{Ib}}{c_{Ia}} \quad (5)$$

and the subscript zero denotes infinite dilution.

It is easily shown that

$$pr - pr_0 = \log \frac{f_{H^+} f_{Ib}}{f_{Ia}} \quad (6)$$

Hence, the addition of these values to the thermodynamic pK_I values will give us $pK_{I(c)}$ at that ionic strength in lithium chloride. From the $pK_{I(c)}$ values of methyl orange, $pK_{A(c)}$ values

of trichloroacetic acid were calculated by using pK values obtained in studying the methyl orange-trichloroacetate system, which were recorded in Table III of the previous paper.¹ From the $pK_{A(c)}$ of trichloroacetic acid, $pK_{I(c)}$ values of all indicators studied in trichloroacetate buffer were calculated. By a continuation of this process, the concentration constants listed in Table IV have been computed.

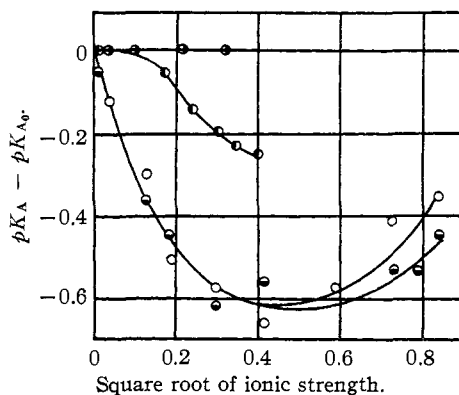


Fig. 1.—Effect of neutral salt on indicators in dilute hydrochloric acid solutions in methanol: ○, tropeoline 00; ●, methyl orange; ●, methyl yellow; ●, thymolbenzein.

In most cases, the salt used at higher ionic strengths was lithium chloride, although sodium bromide was used in some instances. As the difference in the effect of the two salts has been found to be small,¹ no special reference to the salt used has been made in Table IV.

In Fig. 2 are plotted values of $pK_A - pK_{A_0}$ at ionic strengths up to 0.5 M. Here pK_A is the negative logarithm of the concentration constant at a given ionic strength, while pK_{A_0} is the corresponding thermodynamic value.

Discussion

The equation for the curves in Fig. 2 is

$$pK_A - pK_{A_0} = \log f_{H^+} + \log f_B - \log f_A \quad (7)$$

in which A refers to the acid and B to the basic form of the system (either indicator or other acid) studied, while pK_A denotes the negative logarithm of the concentration constant at the stated ionic

TABLE IV
 CONCENTRATION IONIZATION CONSTANTS OF INDICATORS AND ACIDS IN METHANOL

Indicator or acid	Reference acid substance	$pK_{A(c)}$ and $pK_{I(c)}$ at various ionic strengths									
		0.0	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.5
Methyl orange	Hydrochloric	3.8	3.65	3.6	3.5	3.4	3.3	3.3	3.25	3.2	3.25
Tropeoline 00	Hydrochloric	2.2	2.05	2.0	1.9	1.85	1.7	1.6	1.6	1.6	1.7
Trichloroacetic	Methyl orange	4.9	4.75	4.7	4.6	4.5	4.4	4.3	4.1	4.0	4.0
Methyl yellow	Trichloroacetic	3.4	3.4	3.4	3.35	3.35	3.35	3.4	3.4	3.5	3.55
Methyl red (1)	Trichloroacetic	4.1	4.05	4.05	4.0	4.0	3.95	4.0	4.0	4.05	4.1
Thymol blue (1)	Trichloroacetic	4.7	4.55	4.5	4.4	4.3	4.2	4.1			
Thymolbenzein (1)	Trichloroacetic	3.5	3.55	3.6	3.6	3.65	3.7	3.7			
Pentamethoxy red	Trichloroacetic	5.1	5.1	5.1	5.05	5.05	5.05	5.1	5.1	5.1	
Saccharin	Methyl orange	6.1	5.95	5.9	5.8	5.7	5.5	5.4	5.2	5.1	5.05
Brom phenol blue	Saccharin	8.9	8.6	8.5	8.3	8.15	7.85	7.6	7.4	7.3	7.25
Salicylic	Brom phenol blue	7.9	7.75	7.7	7.6	7.5	7.3	7.1	6.95	6.85	
<i>o</i> -Nitrobenzoic	Brom phenol blue	7.6	7.5	7.45	7.3	7.2	7.0	6.8	6.7	6.6	
<i>m</i> -Nitrobenzoic	Brom phenol blue	8.3	8.15	8.1	8.0	7.9	7.7	7.6	7.4	7.3	7.25
<i>p</i> -Nitrobenzoic	Brom phenol blue	8.45	8.3	8.2	8.1	8.0	7.85	7.7	7.5	7.45	7.35
Benzoic	Brom phenol blue	9.4	9.25	9.2	9.1	8.95	8.75	8.6	8.4	8.3	8.25
Anilinium	Brom phenol blue	6.0	5.95	6.05	6.1	6.15	6.1	6.1	6.15	6.2	
Hexamethoxy red	Salicylic	7.25	7.25	7.25	7.2	7.2	7.1	7.1	7.05	7.0	
Neutral red	Salicylic	8.2	8.2	8.25	8.2	8.2	8.25	8.3	8.4	8.45	
Methyl red (2)	Benzoic	9.2	9.05	9.0	8.85	8.75	8.55	8.5	8.5	8.5	8.55
Brom cresol green	Benzoic	9.8	9.5	9.4	9.2	9.05	8.8	8.65	8.4	8.3	8.25
Brom cresol purple	Benzoic	11.3	11.0	10.85	10.7	10.5	10.2	10.05	9.85	9.75	9.65
Acetic	Brom cresol green	9.65	9.55	9.5	9.35	9.25	9.05	8.9	8.75	8.64	8.6
Stearic	Brom cresol green	10.0	9.85	9.8	9.65	9.55	9.35	9.2	9.05	8.95	8.9
Bitartrate	Brom cresol green	9.9	9.55	9.4	9.2	9.0	8.65	8.4	8.1	7.9	
Veronal	Brom cresol purple	12.7	12.55	12.5	12.35	12.2	12.0	11.85	11.65	11.55	11.5
<i>p</i> -Aminobenzoic	Brom cresol purple	10.25	10.05	10.0	9.85	9.7	9.5	9.4	9.2	9.1	9.0
Brom thymol blue	Veronal	12.4	12.1	11.95	11.75	11.55	11.25	11.05	10.85	10.75	10.7
Phenol red	Veronal	12.8	12.5	12.35	12.15	12.0					
Thymolbenzein (2)	Veronal	13.15	13.0	12.95	12.85	12.7	12.5	12.45	12.45		
Thymol blue (2)	Veronal	14.0	13.7	13.6	13.4	13.25	12.95	12.7	12.5	12.4	12.35
Bisuccinate	Brom thymol blue	11.4	11.05	10.9	10.7	10.45	10.1	9.85	9.6	9.45	9.3
Phenol	Thymol blue	14.0	13.9	13.9	13.8	13.7	13.5	13.4			

strength and pK_{A_0} is the corresponding thermodynamic constant.

The limiting Debye-Hückel expression gives us for the activity coefficient f , of an ion in methanol, $-\log f = 2.0z^2\sqrt{\mu}$, in which z is the charge of the ion and μ the ionic strength. As the ionic strength increases, another term must be introduced which is a specific function of the ion in question, the thermodynamic environment and the ionic strength. Thus, at high ionic strength we may write

$$-\log f = 2.0z^2\sqrt{\mu} + B\mu \quad (8)$$

In a given solution, it seems logical to assume that the value of B is the same for an acid and its conjugate base.

An inspection of Fig. 2 reveals that the various systems investigated group themselves into three families of curves. The first group comprises the system, $A^+ \rightleftharpoons B + H^+$. Since $z_B = z_A - 1$, we can write at high dilutions

$$pK_A - pK_{A_0} = 4(z_A - 1)\sqrt{\mu} \quad (9)$$

For the group under consideration, this expression becomes zero at high dilutions. This is found to be the case for methyl yellow, thymolbenzein, anilinium, penta- and hexamethoxytriphenylcarbinols. At higher ionic strengths, small

individual differences are noticed, as is to be expected.

The second group includes the system $A \rightleftharpoons B^- + H^+$. According to equation (9), the slope of the line should be -4 at small ionic strength, which is found. The curves for methyl orange and tropeoline 00 at ionic strengths of the order of 0.01 belong to the same family, but at greater ionic strengths the changes become less than those of other uncharged acid types. This is explained by the hybrid type of the acid forms of the indicator. It was mentioned in a previous paper¹ that, according to a postulate of Bjerrum,³ the charges on a hybrid ion at fairly high ionic strengths are sufficiently displaced to make it behave as two ions. It was found that this postulate could be extended to a hybrid ion with n charges. At high ionic strengths, the activity coefficient of the latter becomes

$$-\log f_n = -n \log f_1 \quad (10)$$

From equations (7), (8), and (10), then, we find at greater ionic strengths

$$pK_A - pK_{A_0} = (B_I - B_{II})\mu \quad (11)$$

in which pK_{A_0} refers to the constant at a certain ionic strength where equation (10) is applicable.

(3) N. Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923).

Actually, it is seen that the curves for methyl orange and tropeoline 00 almost become horizontal at ionic strengths greater than 0.1. This is to be expected, as B_I and B_H will be of the same order of magnitude.

The behavior of methyl red is hard to explain. In acid medium (methyl red I), the $pK_{I(c)}$ change is similar to that of methyl yellow, indicating that the intermediate red form behaves as an uncharged base. But, in its color change from orange to yellow (methyl red II), it behaves similarly to methyl orange and tropeoline 00, indicating a hybrid ion structure of the intermediate form. More work should be done to explain this behavior.

The third group includes the system $A^- \rightleftharpoons B^- + H^+$. To this group belong the bitartrate and bisuccinate, the $pK_{A(c)}$ changes at very small ionic strengths approaching the calculated value of $8\sqrt{\mu}$ (Equation 9). At small ionic strengths, the sulfonphthaleins in their color change from yellow to the alkaline color belong to this group. At greater ionic strength, however, these indicators approach the system $A \rightleftharpoons B^- + H^+$ very closely. This is explained by the hybrid character of the ions.¹ At greater ionic strengths, then, we have

$$pK_I - pK_{I_s} = \log f_{H^+} + \log f_{I_b} - \log f_{I_a} = \log f_{H^+} + \log f_I$$

For the five sulfonphthaleins studied to an ionic strength of 0.5, we find for $pK_{0.1} - pK_{0.5}$ values between 0.35 to 0.40, while this difference fluctuates for trichloroacetic, meta and para nitrobenzoic, benzoic, acetic, stearic acids, saccharin, and veronal between 0.30 and 0.35.

From the above, it is seen that the changes of the concentration constants of the various indicators and acids studied, with the exception of methyl red, can be interpreted on the basis of the modern views of the theory of interionic attraction.

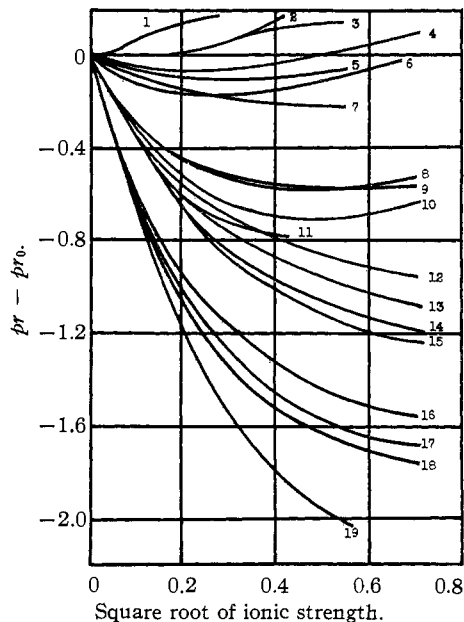


Fig. 2.—Change of pK_A with increasing ionic strength.

- | | |
|--------------------------|---|
| 1. Thymolbenzein (1) | 13. Saccharin; salicylic acid |
| 2. Neutral red | 14. Benzoic acid |
| 3. Aniline | 15. Veronal |
| 4. Methyl yellow | 16. Brom cresol green |
| 5. Pentamethoxy red | 17. Thymolblue(2); brom phenol blue; brom cresol purple |
| 6. Methyl red (1) | 18. Brom thymol blue; phenol red |
| 7. Hexamethoxy red | 19. Bisuccinate; bitartrate |
| 8. Tropeoline 00 | |
| 9. Methyl orange | |
| 10. Methyl red (2) | |
| 11. Thymolbenzein (2) | |
| 12. Trichloroacetic acid | |

Summary

1. "Concentration ionization constants" of a number of indicators and acids in methanol have been evaluated.
2. The variation of these constants as a function of the ionic strength has been interpreted in the light of the theory of interionic attraction.

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