[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

Ionization Constants of Acid–Base Indicators in Methanol

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The equilibrium constant in a buffer system containing a small amount of an acid–base indicator is given by the expression

$$K' = \frac{(aI_b)(aA)}{(aI_a)(aB)} = \frac{cI_b\ cA}{cI_a\ cB}\ \frac{f_{1b}\ f_A}{f_{1a}\ f_B} = K\ \frac{f_{1b}\ f_A}{f_{1a}\ f_B} \quad (1)$$

in which a denotes the activity of the component, c the concentration, I_b the basic form and I_a the acid form of the indicator, A and B the acid and basic forms of the buffer, K' the thermodynamic equilibrium constant, while K is the corresponding and experimentally determinable concentration "constant," the value of which varies with the ionic strength of the solution. By extrapolating the values of K found at small ionic strengths to an ionic strength of zero, the value of K' is found. This method of evaluation of K' is similar to that used by Guggenheim and Schindler[2] in aqueous solutions.

In sufficiently dilute solution, the limiting Debye–Hückel expression gives the relation between activity coefficient and ionic strength. In methanol at 25°, this becomes

$$-\log f_{\text{ion}} = 2.0z^2\sqrt{\mu} \quad (2)$$

In the range in which the limiting expression is applicable, equation 1 gives us

$$pK' = pK - \log\frac{f_{1b}\ f_A}{f_{1a}\ f_B} = pK - 4.0(z_{1a} - z_A)\sqrt{\mu} \quad (3)$$

where z_{1a} and z_A are the charges of the indicator acid and the buffer acid, respectively. If the values of pK are plotted against the square root of the ionic strength, the slope of the curve should be $4(z_{1a} - z_A)$ in the range where the limiting expression holds. Table I lists values of this slope for various types of indicator and buffer acids.

TABLE I

VALUES OF $4.0(z_{1a} - z_A)$

	Type of indicator acid		
Type of buffer acid	Cation	Uncharged	Anion
Cation	0.0	−4.0	−8.0
Uncharged	4.0	0.0	−4.0
Anion	8.0	4.0	0.0

Having obtained by extrapolation the value of pK, the thermodynamic ionization constant, K_1, of the indicator can be calculated if the dissociation constant of the acid, K_A, is known since

$$pK_1 = pK' + pK_A$$

Although there are many data in the literature on the acidity constants and concentration ionization constants of acids in methanol, only few studies have been carried out at sufficiently small ionic strengths to allow the determination of the thermodynamic ionization constant. In the present work, the values of Goldschmidt and coworkers,[3] who determined the constants by the conductivity method, have been adopted as the most reliable values. The constant of veronal, which is not given in the literature, has been determined by the colorimetric procedure described in this paper, using the pK_1 value which has been found previously in another buffer. In a similar way, the ionization constants of other acids in methanol have been determined.

Experimental

Reagents.—A good grade of synthetic methanol free of aldehydes was dehydrated by the method of Lund and Bjerrum[4] followed by distillation over sulfanilic acid to remove traces of alkaline impurities. The density of the final product was measured with a 100 ml. pycnometer. Freshly distilled products gave values of d^{25}_4 0.78651. No sample whose density was above 0.78661^{25}_4 was used, the latter value corresponding to less than 0.04% water. The presence of a trace of water has a negligible effect on indicator equilibria in buffered solutions.

The sulfonphthaleins were furnished through the courtesy of Hynson, Westcott and Dunning and were used without further purification. Thymolbenzein was obtained from a collection of the late Dr. W. R. Orndorff of Cornell University. Other indicators were purified by conventional methods.

Lithium chloride was precipitated from a saturated solution in methanol by hydrogen chloride, then fused in platinum in an atmosphere of hydrogen chloride. Sodium bromide and sodium nitrate were recrystallized from water and dried to constant weight at 110°. All other reagents were purified by conventional methods.

Sodium methoxide solutions were prepared by dropping pure sodium into methanol and, after solution was complete, diluting up to the desired strength. Solutions of acids were prepared by weight and checked by titration with sodium hydroxide. Solutions of lithium chloride and

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(1) From the dissertation submitted by L. S. Guss to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1938.

(2) E. A. Guggenheim and T. D. Schindler, *J. Phys. Chem.*, **38**, 543 (1934).

(3) H. Goldschmidt and H. Aarflott, *Z. physik. Chem.*, **117**, 317 (1925); H. Goldschmidt and E. Mathiesen, *ibid.*, **119**, 453 (1926); H. Goldschmidt and F. Aas, *ibid.*, **112**, 429 (1924).

(4) H. Lund and J. Bjerrum, *Ber.*, **64B**, 210 (1931); see also N. Bjerrum and L. Zechmeister, *ibid.*, **56B**, 894 (1923).

sodium bromide were prepared similarly and checked by titration with silver nitrate.

Method.—Accurately measured volumes of a solution of the suitable buffer acid and of sodium methoxide were introduced into a test-tube to give an intermediate color to the indicator investigated. If desired, a certain amount of a neutral salt was added to obtain a certain ionic strength, then 0.05 ml. of 0.04% indicator solution and the mixture made up to 5.0 ml. with methanol. The fraction of the indicator in the alkaline form was then measured by the method of Gillespie[5] and the value of pK calculated from the ratio of the concentration of acid and basic forms of the indicator and the composition of the buffer. These values were then plotted against the square root of the ionic strength, and extrapolated to zero concentration, using the limiting Debye–Hückel expression for the final extrapolation.

Results.—For example, a solution was 0.02 N in benzoic acid, 0.0199 N in sodium benzoate, 0.20 M in lithium chloride and 0.01% in brom cresol green (added as the sodium salt). The ratio of cI_b/cI_a was found to be 0.96 and the ratio of cB/cA in the buffer was 0.99. Hence

$$K = 0.96/0.99 = 0.975$$

and $pK = 0.01$.

As an illustration, in Table II are listed the data obtained in a study of the behavior of brom phenol blue in salicylate buffers. The results of other determinations have been summarized in Table III. The values of pK given were obtained by interpolation from curves in which pK was plotted against the square root of the ionic strength. The first column gives the values obtained on extrapolating to zero ionic strength. The superscripts refer to neutral salts in the solution, 1 referring to lithium chloride, 2 to sodium bromide and 3 to sodium nitrate.

TABLE II

BROM PHENOL BLUE IN SALICYLATE BUFFER

$c_{\text{Salicylate}}$	Salt added	c_{Salt}	$\sqrt{\mu}$	cB/cA	cI_b/cI_a	pK
0.00036			0.019	3.34	0.43	0.89
.00036			.019	5.9	.725	.91
.0005			.022	3.34	.43	.89
.0009			.030	3.34	.47	.85
.0009			.030	5.9	0.82–0.73	0.86–0.91
.0022			.047	3.34	0.54	0.79
.0022			.047	5.9	.925	.80
.0056			.075	3.34	.61	.74
.0056			.075	5.7	1.00–1.08	0.76–0.72
.012			.11	2.03	0.54–0.59	.58– .54
.014			.12	3.34	0.67	0.70
.014			.12	5.9	1.38	.63
.016			.13	8.4	2.33	.56
.006	$NaNO_3$	0.003	.095	2.04	0.43	.68
.006	$NaNO_3$	.006	.11	2.04	.49	.62
.006	$NaNO_3$	.015	.145	2.04	.54	.58
.006	$NaNO_3$	.024	.175	2.04	.615	.52
.006	$NaNO_3$	.030	.19	2.04	.67	.49
.006	$NaNO_3$	.045	.225	2.04	.67	.49
.006	$NaNO_3$	.060	.26	2.04	.67	.49
.006	$NaNO_3$	.090	.31	2.04	.725	.45
.006	LiCl	.014	.14	2.04	.47	.64
.006	LiCl	.027	.18	2.04	.54	.58
.006	LiCl	.041	.22	2.04	.67	.49
.006	LiCl	.069	.275	2.04	.67	.49
.006	LiCl	.137	.38	2.04	.695	.47
.006	LiCl	.274	.53	2.04	.725	.45

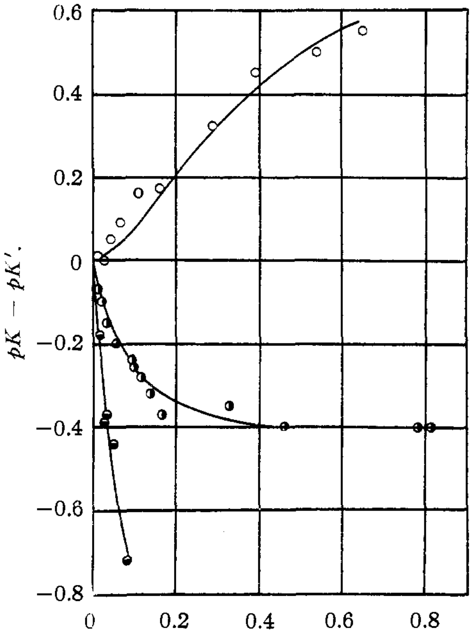

Fig. 1.—Brom cresol green in ○, tartrate, ◑, benzoate, and ⊖, ammonium buffers.

The behavior of various indicator–buffer systems is shown more clearly in the figures. Figure 1 shows the behavior of brom cresol green in its alkaline range in various types of buffers. This behavior is typical of the sulfonphthaleins. For convenience, $pK - pK'$ has been plotted against the square root of the ionic strength. In Fig. 2, the behavior of the azo indicators, methyl yellow and methyl orange is illustrated. Figure 3 shows the behavior of methyl red in its two color change intervals. Figure 4 illustrates the two color changes of thymolbenzein and of thymol blue in its acid range.

Discussion

1. The sulfonphthaleins in their alkaline range approach the behavior predicted on the basis of the limiting Debye–Hückel expression, as the ionic strength approaches zero. This is evidenced by the slope of the lines given in Fig. 1. With increasing ionic strength, the pK values vary in some regular way. With buffers of the type A–B$^-$ (A is an uncharged acid, B$^-$ is the

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[5] L. J. Gillespie, THIS JOURNAL, **42**, 742 (1920).

TABLE III

VALUES OF *pK* IN VARIOUS INDICATOR–BUFFER SYSTEMS

Indicator	Buffer	Ionic strengths									
		0.0	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.5
Brom phenol blue	Salicylate	1.0	0.8	0.75	0.7	0.65^{1} $.6^{3}$	0.5^{13}	0.45^{13}	0.45^{13}		
Brom phenol blue	*o*-Nitrobenzoate	1.3	1.1	1.0	1.0	.9	.85	$.8^{1}$	$.75^{1}$	0.75^{1}	
Brom phenol blue	*m*-Nitrobenzoate	0.6	0.45	0.35	0.3	.25	$.1^{1}$	$.05^{1}$	$.0^{1}$	$.0^{1}$	
Brom phenol blue	*p*-Nitrobenzoate	.5	.3	.25	.2	.1	$.0^{1}$	$-\ .05^{1}$	$-\ .1^{1}$	$-\ .1^{1}$	
Brom cresol green	Benzoate	.4	.25	.2	.15	$.1^{12}$	$.05^{12}$	$.0^{12}$	$.0^{12}$	$.0^{12}$	0.0^{12}
Brom cresol green	Acetate	.15	.0	− .1	− .15	$-\ .2^{12}$	$-\ .2^{12}$	$-\ .25^{1}$ $-\ .3^{2}$	$-\ .3^{12}$	$-\ .35^{12}$	$-\ .35^{12}$
Brom cresol green	Stearate	− .2	− .35	− .4	− .45	$-\ .5^{2}$	$-\ .55^{2}$	$-\ .55^{2}$	$-\ .6^{2}$	$-\ .6^{2}$	$-\ .6^{2}$
Brom cresol purple	Benzoate	1.9	1.7	1.65	1.6	1.55	1.45^{2}	1.4^{2}	1.4^{2}	1.4^{2}	1.45^{2}
Brom cresol purple	*p*-Aminobenzoate	1.05	0.9	0.85	0.8	0.7	0.65^{2}	0.6^{2}	0.6^{2}	0.6^{2}	0.6^{2}
Brom thymol blue	Veronalate	−0.3	− .45	− .5	$-\ .6^{2}$ $-\ .65^{1}$	$-\ .65^{2}$ $-\ .75^{1}$	$-\ .7^{2}$ $-\ .75^{1}$	$-\ .7^{2}$ $-\ .8^{1}$	$-\ .7^{2}$ $-\ .85^{1}$	$-\ .65^{2}$ $-\ .85^{1}$	$-\ .5^{2}$ $-\ .85^{1}$
Phenol red	Veronalate	.1	− .05	− .15	− .2	− .3					
Thymol blue	Veronalate	1.3	1.2	1.1	1.05	1.0	$.95^{1}$	$.9^{1}$	$.85^{1}$	$.85^{1}$	$.85^{1}$
Thymol blue	Phenolate	0.0	−0.15	−0.25	−0.35	−0.45	$-\ .55^{1}$	$-\ .65^{1}$			
Thymol blue	Trichloroacetate	− .2	− .2	− .2	− .2	− .2	-0.2^{1}	-0.2^{1}			
Brom thymol blue	Succinate	1.0	1.05	1.05	1.05	1.1	1.15^{2} 1.25^{1}	1.2^{2} 1.3^{1}	1.25^{2} 1.35^{1}	1.25^{2} 1.35^{1}	1.3^{2} 1.4^{1}
Brom cresol green	Tartrate	−0.1	−0.05	0.0	0.05	0.1	0.15^{1}	0.25^{1}	0.35^{1}	0.4^{1}	
Brom cresol green	Ammonium	−0.9	−1.3	−1.55							
Brom phenol blue	Anilinium	2.9	2.5	2.3	2.15	1.95^{1}	1.75^{1}	1.5^{1}	1.3^{1}	1.15^{1}	
Methyl orange	Trichloroacetate	−1.1	−1.1	−1.1	−1.1	-1.1^{1}	-1.05^{1}	-1.0^{12}	-0.85^{12}	-0.8^{12}	-0.75^{12}
Methyl red	Benzoate	−0.2	−0.2	−0.2	−0.2	−0.2	-0.15^{1}	-0.05^{2}	$.0^{12}$	$.1^{12}$	$.25^{12}$
Methyl red	Trichloroacetate	− .8	− .7	− .65	− .6	− .55	$-\ .45^{1}$	$-\ .3^{1}$	$-\ .1^{1}$	$.0^{1}$	$.15^{1}$
Methyl yellow	Trichloroacetate	−1.5	−1.35	−1.3	−1.25	-1.15^{1}	-1.0^{12}	$-\ .95^{1}$ $-\ .75^{2}$	$-\ .75^{1}$ $-\ .55^{2}$	$-\ .65^{1}$ $-\ .45^{2}$	$-\ .5^{1}$ $-\ .4^{2}$
Neutral red	Salicylate	0.3	0.45	0.55	0.6	0.75	0.95^{12}	1.2^{12}	1.45^{1} 1.55^{2}	1.6^{2}	1.75^{2}
Methyl yellow	*o*-Chloroanilinium	.0	.0	.0	.0	$.0^{1}$	$.0^{1}$	$.0^{1}$	0.0^{1}	0.0^{1}	0.0^{1}
Methyl orange	*o*-Chloroanilinium	− .15	− .15	− .15	− .15	− .2	− .2	$-\ .2^{2}$	$-\ .25^{2}$	$-\ .2^{2}$	$-\ .2^{2}$
Thymolbenzein	Trichloroacetate	−1.4	−1.25	−1.1	-1.0^{2}	$-\ .9^{2}$	$-\ .7^{2}$	$-\ .55^{2}$			
Thymolbenzein	Veronalate	0.45	0.45	0.45	0.45^{1}	$.5^{1}$	$.6^{1}$	$.75^{1}$	$.75^{1}$		

corresponding univalent anion base), a limiting slope of −4 is obtained. With increasing ionic strength, the *pK* values decrease less than demanded by the limiting expression. This is to be expected as the latter in methanol will only be valid at very small ionic strengths. When the ionic strength has become of the order of 0.06, the *pK* values remain practically constant with increasing ionic strength. This behavior is typical of all of the sulfonphthaleins and can be interpreted on the basis of the structures of the sulfonphthaleins as originally proposed by Lund[6] and supported by the work of Schwarzenbach.[7] According to Lund, the structural changes of a sulfonphthalein in its various color change intervals is represented by

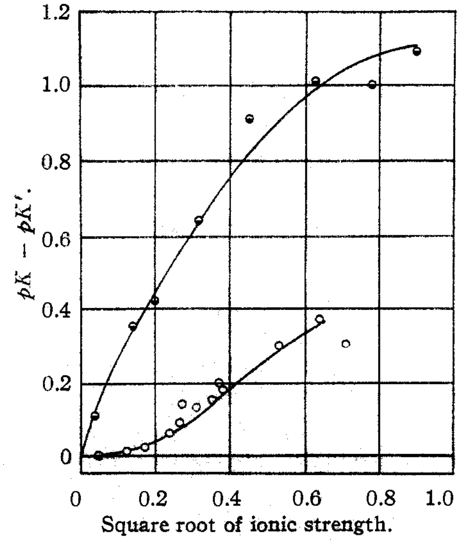
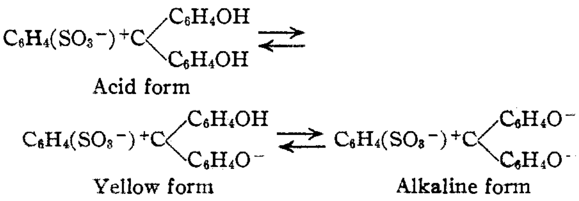


Fig. 2.—○, Methyl orange and ◒, methyl yellow in trichloroacetate buffer.



$$C_6H_4(SO_3^-)^+C\begin{matrix}C_6H_4OH\\ C_6H_4OH\end{matrix} \rightleftharpoons$$

$$C_6H_4(SO_3^-)^+C\begin{matrix}C_6H_4OH\\ C_6H_4O^-\end{matrix} \rightleftharpoons C_6H_4(SO_3^-)^+C\begin{matrix}C_6H_4O^-\\ C_6H_4O^-\end{matrix}$$

Thus, the yellow form is a hybrid ion with one extra negative charge and the alkaline form a hybrid ion with two extra negative charges. Bjerrum[8] postulated that the charges on a hybrid ion are sufficiently displaced that, in a fairly concentrated solution, it behaves as two ions. Güntel-

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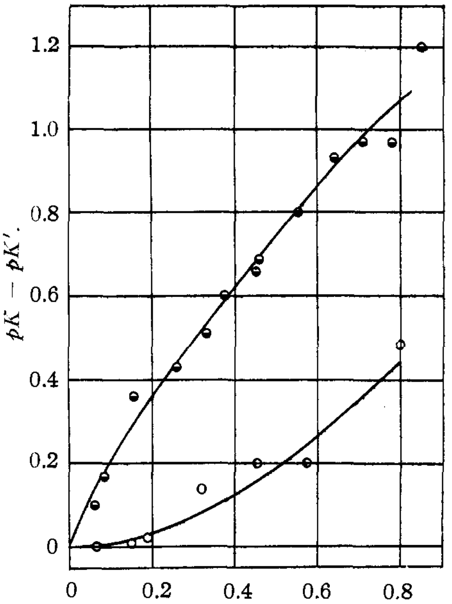
[6] H. Lund, *J. Chem. Soc.*, 1844 (1930).

[7] G. Schwarzenbach, *Helv. Chim. Acta*, **20**, 490 (1937), *et seq.*

[8] N. Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923).



Square root of ionic strength.

Fig. 3.—Methyl red in ○, benzoate and ⊖, trichloroacetate buffers.

berg and Schiödt[9] showed that the behavior of methyl orange with varying ionic strength could be explained by such a hypothesis. The same reasoning should apply to any highly charged ion, with widely displaced charges. Thus, we might assume that at higher ionic strengths the electrical work required to build up n individual charges will be n times as great as that required to build up a single charge. In the yellow form of the sulfonphthaleins, n is equal to 3 and in the alkaline form, equal to 4. At high ionic strengths, we then may write the following relation for the activity coefficient

$$-\log f_n = -n \log f_1 \qquad (4)$$

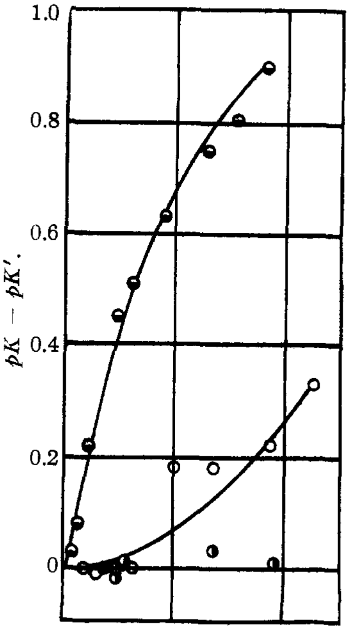
in which f_1 is the activity coefficient of a univalent ion.

For univalent ions in fairly concentrated solutions, the Debye–Hückel expression might be written

$$-\log f_1 = f(\sqrt{\mu}) + B \qquad (5)$$

where B is some function of the ionic strength. It seems fair to assume that B will be of the same magnitude for ions of a conjugate acid–base system. Applying the above to the sulfonphthaleins in buffers of the type A–B$^-$ at higher ionic strength, we find

$$\begin{aligned} pK &= pK'' - \log f_{\equiv} + \log f_{\overset{=}{=}} - \log f_- + \log f_0 \\ &= pK'' - 3 \log f_1 + 4 \log f_1 - \log f_1 = pK'' \qquad (6) \end{aligned}$$



Square root of ionic strength.

Fig. 4.—Thymolbenzein in ○, veronalate, and ⊖, trichloroacetate and ◑, thymol blue in trichloroacetate.

in which pK'' is not the true thermodynamic constant since the relation in equation 4 will not permit extrapolation down to infinite dilution. According to the above interpretation, pK becomes constant at relatively high ionic strengths, which is in agreement with experimental results.

The above considerations are also of practical importance. If the pK values of sulfonphthaleins in various alcohols are determined in buffer solutions of the type A–B$^-$ with an ionic strength of about 0.1, the result of a 5- to 10-fold dilution will be a very small effect upon the pK measured. Extrapolation of those data to an ionic strength of zero, however, would lead to an erroneous result. Kolthoff,[10] who investigated the sulfonphthaleins in ethanol, has applied such an extrapolation. From this discussion, it is clear that his data need correction.

In buffers of the type A$^-$–B$^=$, the pK values of the sulfonphthaleins should become constant and independent of the ionic strength when the latter is very small. Actually, this was found to be the case with brom cresol green in bitartrate–tartrate buffers at ionic strengths below 0.001. When the ionic strength becomes greater than

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[9] E. Güntelberg and E. Schiödt, *Z. physik. Chem.* **135**, 393 (1928).

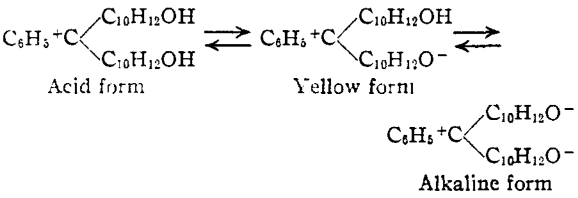
[10] I. M. Kolthoff, *J. Phys. Chem.*, **35**, 2732 (1931).

this, the pK values increase. This is in agreement with the above considerations.

The tremendous effect of the ionic strength upon the pK values in buffers of the type A$^+$–B is also in agreement with the predictions based on the above discussion. At low ionic strengths, the curve has the slope of -8 required by equation 3 (see Fig. 1). At higher ionic strengths, the theory of individual charges seems again applicable.

The behavior of thymol blue in its acid range is in agreement with the structure proposed by Lund. The pK values found in trichloroacetate buffer were found to be constant up to an ionic strength of 0.1.

2. In connection with what has been said of the sulfonphthaleins, the behavior of thymolbenzein in its two color changes is of interest. On the basis of the work of Lund and Schwarzenbach, the structural changes may be represented by



In its acid range, in a buffer of the type A–B$^-$, we would have

$$pK = pK'' - \log f_+ + \log f_{\mp} - \log f_- + \log f_0$$

At small ionic strengths, this leads to

$$pK = pK' + 4\sqrt{\mu}$$

The slope of 4 actually was observed in trichloroacetate buffers. At high ionic strengths, we would expect to find $pK = pK''$ and independent of μ. Although the slope did increase, it still had a positive value at an ionic strength of 0.126.

In the alkaline range, with the same type of buffer, the following relation should hold at higher ionic strengths

$$pK = pK'' - \log f_{\mp} + \log f_{\mp} - \log f_- + \log f_0 = pK''$$

Actually the pK was found to be constant up to an ionic strength of about 0.01. Above this, pK increased. More work should be done in order to interpret the behavior of the benzeins at higher ionic strengths.

3. The behavior of azo indicators and of neutral red in buffers of the type A–B$^-$ is in agreement with the postulates given in the introduction of this paper. The slope of the pK line of methyl yellow against the square root of the ionic strength in trichloroacetate buffers and of neutral red in salicylate buffers approaches the value calculated on the basis of the limiting Debye–Hückel expression (Table I and Fig. 2). At greater ionic strengths, the pK values of both indicators increase less than calculated on the basis of the limiting expression, which is to be expected since the latter disregards ionic diameter. With both indicators, the deviations are greater with lithium chloride than with sodium bromide.

The behavior of methyl orange in trichloroacetate buffer (Fig. 2) is explained readily by the hybrid character of the acid form of the indicator. At small ionic strengths, the pK values become constant, but pK increases at greater ionic strengths. In the latter case we have

$$pK = pK'' - \log f_{\mp} + \log f_- - \log f_- + \log f_0 = pK'' - 2 \log f_1$$

While the behavior of methyl yellow in *o*-chloroanilinium buffer is quite normal, the behavior of methyl orange in the same buffer is abnormal. A limiting slope of pK against the square root of the ionic strength of 4 was expected, but as seen from the data in Table III, the pK was found to be sensibly independent of ionic strength. Whether this result is to be attributed to a specific interaction between methyl orange and the buffer has not been investigated.

Methyl red has two color changes, in the acid range from red to orange and in the alkaline range from orange to yellow. The latter corresponds to the color change in water from so-called Red II to yellow, but is less pronounced in methanol. In the acid range (trichloroacetate buffer), the change of the pK at small ionic strengths is similar to that of methyl yellow and neutral red (see Fig. 3), but at higher ionic strengths the pK does not increase as much as that of other indicators. In the alkaline range (benzoate buffers), the pK becomes constant at small ionic strengths and increases at larger ionic strengths. The salt effect is almost identical with that of methyl orange in trichloroacetate buffer. The salt effects in the acid and alkaline ranges are best explained on the assumption that the orange form (comparable with Red II in water) is present as a neutral amino acid and not as a hybrid ion. This behavior is in agreement with the change of the indicator constant, pK_I, on going from water to methanol. The pK_I of methyl red in water is 5.0, and in methanol ($pK_{I(2)}$), 9.2. The change of 4.2 cor-

TABLE IV

EFFECT OF WATER ON INDICATOR EQUILIBRIA IN BUFFER SOLUTIONS

Buffer	Indicator	cI_b/cI_a In pure methanol	With 1% water
Trichloroacetate	Methyl yellow	2.33	2.33
Trichloroacetate	Methyl orange	1.50	1.55
Benzoate	Brom cresol green	1.13	1.22
Veronalate	Brom thymol blue	0.64	0.615
Veronalate	Brom cresol purple	0.43	0.41
Veronalate	Phenol red	1.00	1.00
Succinate	Brom cresol purple	0.92	0.82

TABLE V

DISSOCIATION CONSTANTS OF INDICATORS IN METHANOL

Indicator	Buffer	pK_A	pK'	$pK_{I(MeOH)}$	$pK_{I(H_2O)}$
Tropeoline 00	Hydrogen chloride			2.2	2.0
Methyl yellow	Trichloroacetate	4.9	−1.5	3.4	3.25
Thymolbenzein (1)	Trichloroacetate	4.9	−1.4	3.5	
Methyl orange	Trichloroacetate	4.9	−1.1	3.8	3.45
Methyl red (1)	Trichloroacetate	4.9	−0.8	4.1	2.3
Thymol blue (1)	Trichloroacetate	4.9	− .2	4.7	1.65
Neutral red	Salicylate	7.9	− .3	8.2	7.4
Neutral red	Acetate	9.65	−1.4	8.25	7.4
Brom phenol blue	Salicylate	7.9	1.0	8.9	4.1
Brom phenol blue	Benzoate	9.4	−0.4	9.0	4.1
Methyl red (2)	Benzoate	9.4	− .2	9.2	5.0
Brom cresol green	Benzoate	9.4	.4	9.8	4.9
Brom cresol purple	Benzoate	9.4	1.9	11.3	6.4
Brom thymol blue	Veronalate	12.7	−0.3	12.4	7.3
Phenol red	Veronalate	12.7	+ .1	12.8	8.0
Thymolbenzein (2)	Veronalate	12.7	.45	13.15	
Thymol blue (2)	Veronalate	12.7	1.3	14.0	9.2

TABLE VI

DISSOCIATION CONSTANTS OF SOME ACIDS IN METHANOL

Acid	Indicator	pK_I	pK'	pK_A	$pK_{A(H_2O)}$
o-Nitrobenzoic	Brom phenol blue	8.9	1.3	7.6	2.2
m-Nitrobenzoic	Brom phenol blue	8.9	0.6	8.3	3.5
p-Nitrobenzoic	Brom phenol blue	8.9	.5	8.4	3.4
Acetic	Brom cresol green	9.8	.15	9.65	4.75
Stearic	Brom cresol green	9.8	− .2	10.0	
p-Aminobenzoic	Brom cresol purple	11.3	1.05	10.25	4.8
Veronal	Brom cresol green	9.8	−2.8	12.6	7.4
Veronal	Brom cresol purple	11.3	−1.4	12.7	7.4
Phenol	Thymol blue	14.0	0.0	14.0	9.9
o-Chloroanilinium	Methyl yellow	3.4	.0	3.4	3.25
o-Chloroanilinium	Methyl orange	3.8	− .15	3.95?	3.25
Anilinium	Brom phenol blue	8.9	2.9	6.0	4.6
Ammonium	Brom cresol green	9.8	−0.9	10.7	9.25
Bitartrate	Brom cresol green	9.8	− .1	9.9	4.55
Bisuccinate	Brom cresol purple	11.3	− .1	11.4	5.6
Bisuccinate	Brom thymol blue	12.4	1.0	11.4	5.6
Biphthalate	Brom cresol purple	11.3	−0.35	11.65	5.4

responds to that of an uncharged carboxylic acid. On the other hand, the behavior of methyl orange in this respect (3.5 in water, 3.8 in methanol) indicates conclusively the hybrid ion structure of the acid form. From their work on the indicator constants in water–ethanol mixtures, Baggesgaard-Rasmussen and Reimers[11] arrived at the conclusion that the Red II form of methyl red or the orange form in alcohol has the amino acid and not the hybrid ion structure. Kolthoff[12] and Thiel[13] came to the opposite conclusion from a consideration of the salt effect in water. In agreement with the former conclusion is the fact that the temperature has hardly any effect on the intermediate color of methyl red in a benzoate buffer in water or in methanol. If the orange form had a hybrid structure the color should shift to a yellow on increasing the temperature.

4. The effect of small amounts of water

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(11) H. Baggesgaard-Rasmussen and F. Reimers, *Dansk. Tidsskr. Farm.*, **7**, 225 (1933).

(12) I. M. Kolthoff, *Rec. trav. chim.*, **44**, 68 (1925).

(13) A. Thiel, A. Dassler and F. Wülfken, *Ber.*, **56**, 1667 (1923).

should be negligibly small as long as the concentration of the water is not great enough to affect the properties of the solvent appreciably. From a large number of experiments, a few examples of which are listed in Table IV, it is seen that the presence of 1% water in a buffer solution hardly affects the indicator–buffer equilibrium.

In Table V is given a summary of the values of the negative logarithms of the ionization constants of indicators, *pK*I, at an ionic strength of zero. The values, naturally, are no more reliable than the *pK*A values from which they were calculated. The *pK*I of Tropeoline 00 has been obtained from experiments in dilute hydrochloric acid solutions in methanol, which will be reported in a subsequent publication.

In Table VI is given a list of the *pK*A values of various acids at $\mu = 0$, which were calculated from the extrapolated pK' values and the *pK*I values of Table V.

Summary

1. Thermodynamic ionization constants of a number of indicators and of acids have been determined in methanol, and the effect of ionic strength studied.

2. The behavior of the sulfonphthaleins and thymolbenzein is in agreement with modern views of their structures.

3. In agreement with Baggesgaard-Rasmussen and Reimers, it was found that the behavior of methyl red is best explained on the basis of the existence of the free amino acid form, and not of the hybrid form, although the salt effect is not entirely accounted for by this interpretation.

4. The behavior of other indicators is in agreement with present concepts. At very small ionic strengths, the salt effect can be accounted for quantitatively by the limiting Debye–Hückel expression.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Specific Heats and Heat of Fusion of Tellurium Tetrachloride

BY K. J. FREDERICK AND J. H. HILDEBRAND

A calculation of the internal pressure of tellurium tetrachloride by the senior author[1] shows that this tetrachloride differs from all others in the magnitude of its molecular field, which is near to that of iodine. It is to be expected, therefore, that solutions of these two substances with each other should be nearly ideal, provided that they do not react and that the former does not have a more or less ionic field, which may prove to be the case. The freezing point diagram for this system is now being constructed in this Laboratory. In order to evaluate the data, however, it is necessary to have reliable figures for the specific heats and heats of fusion. Data for iodine recently have been reported by us[2] and this paper presents similar results for tellurium tetrachloride, for which no determinations of the quantities are to be found in the literature.

Preparation and Purification of Sample.—The material used was purified by fractional distillation, the final fraction distilling at a mean temperature of 390° under atmospheric pressure. Its melting point was 224.1°. The purified material was enclosed in small Pyrex glass capsules, evacuated before sealing. The capsules had an external diameter of 12 mm., an internal diameter of 10 mm., and a length of approximately 6 cm. The ratio of weight of tellurium tetrachloride to weight of glass was about 1.4. Two different capsules were prepared and each one was used in a considerable number of the runs. The average free space in the capsules was 1.7 cc. Calculations indicate that the tellurium tetrachloride vapor in the capsules was a negligible factor.

Method.—The apparatus and method used in these determinations were the same as described in the account of the work with iodine. The higher melting point of the tellurium tetrachloride necessitated further calibration of the thermocouple in the furnace and the melting point of tin was used for this purpose.

Results and Discussion.—The value of the heat capacity of the calorimeter was 11.3 ± 0.4 cal. per degree. Runs on the Pyrex glass used in making the capsules showed that its specific heat for the interval 25–250° could be

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(1) J. H. Hildebrand, "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 1936.

(2) Frederick and Hildebrand, THIS JOURNAL, **60**, 1436 (1938).