Ionization Constants of Acid–Base Indicators in Ethanol

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

In a buffer system containing the acid–base system, A and B and the indicator system I_a and I_b, we define a concentration equilibrium constant by the equation:

$$K = \frac{c_{I_b}\, c_A}{c_{I_a}\, c_B} \tag{1}$$

and a thermodynamic constant, K', by a similar equation using activities in place of concentrations

$$K' = \frac{a_{I_b}\, a_A}{a_{I_a}\, a_B} = K \frac{f_{I_b} f_A}{f_{I_a} f_B} \tag{2}$$

According to the limiting Debye–Hückel expression

$$-\log f_{iou} = \alpha z^2 \sqrt{\mu} \tag{3}$$

From equations (2) and (3), it follows that

$$pK = pK' + 2\alpha(z_{I_a} - z_A)\sqrt{\mu} \tag{4}$$

where z refers to the charges on the respective molecules. The value of α in water at 25° is 0.5, in methanol, 2.0, and in ethanol, 2.9. Hence, any variation between pK values and ionic strength in water will be magnified by four times in methanol and almost six times in ethanol.
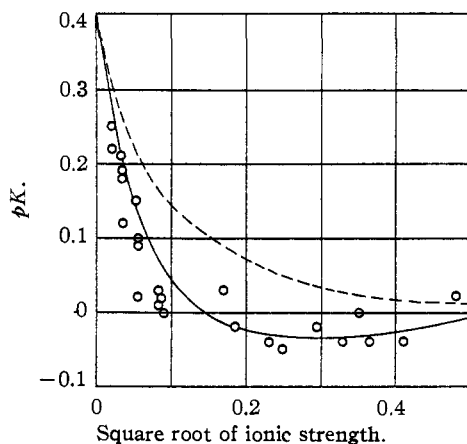

Fig. 1.—Brom cresol green in benzoate buffer. Broken line illustrates corresponding data in methanol.

In a previous study[1] it was shown that equation (4) accounts quantitatively for the change with the ionic strength as long as the latter is small. In his study of indicators in ethanol, Kolthoff[2] hardly found a change of the color equilibrium of

sulfonephthaleins in buffers composed of an uncharged acid and a univalent anion base upon dilution from an ionic strength of 0.1 to 0.01. Erroneously, he concluded that dissociation constants remain unchanged on going from infinite dilution to finite concentrations. It is the purpose of this investigation to correct these data in the light of the above discussion and to consider the effect of varying ionic strength on some indicator–buffer equilibria.

Experimental

Reagents.—A good grade of synthetic ethanol, free of aldehydes, was dehydrated by the method of Lund and Bjerrum,[3] followed by distillation over sulfanilic acid. As in the case of methanol, final purity was checked by density measurements with a 100-ml. pycnometer. All alcohol used contained less than 0.05% water. As
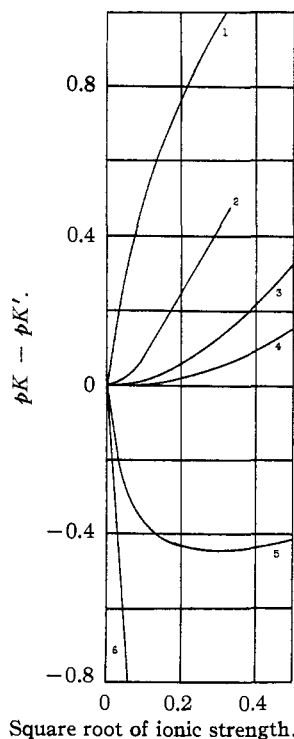

Fig. 2.—Indicator-buffer systems in ethanol: (1) methyl yellow, methyl red, and thymolbenzein in trichloroacetate, neutral red in salicylate; (2) thymolbenzein in veronalate; (3) methyl orange in trichloroacetate; (4) methyl red in benzoate; (5) sulfonphthaleins in uncharged acid buffers; (6) brom cresol green in ammonium.

(1) I. M. Kolthoff and L. S. Guss, THIS JOURNAL, **60**, 2516 (1938).
(2) I. M. Kolthoff, J. Phys. Chem., **35**, 2732 (1931).
(3) H. Lund and J. Bjerrum, Ber., **64B**, 210 (1931).

pointed out before,[1] the presence of a trace of water will have no effect on these buffered solutions.

Indicators and acids were purified by methods already described. Ionic strength was controlled by the addition of lithium chloride, precipitated from methanol solution by the addition of hydrogen chloride and fused in platinum in an atmosphere of hydrogen chloride. Sodium ethoxide was prepared by dropping pure sodium into ethanol, the solutions showing no discoloration.

Method.—The general method was that used in the solvent methanol.[1] Values of pK for a given buffer–indicating system were determined over an ionic strength range from about 5×10^{-4} to 0.1. Ionic strengths of 0.01 and less are due to the salt in the buffer, a greater ionic strength being obtained by the addition of lithium chloride. The values of pK were plotted against the square root of the ionic strength and the curve extrapolated to infinite dilution, the final slopes of the curves agreeing with equation (4).

TABLE I
VALUES OF pK IN VARIOUS INDICATOR–BUFFER SYSTEMS IN ETHANOL

Indicator	Buffer	0.0	0.002	0.005	Ionic strengths 0.01	0.02	0.05	0.1
Brom phenol blue	Salicylate	0.8	0.55	0.45	0.45	0.45	0.4	0.4
Brom phenol blue	o-Nitrobenzoate	1.0	.75	.6	.6	.55	.55	.55
Brom phenol blue	m-Nitrobenzoate	0.4	.15	.1	.1	.15	.15	.15
Brom phenol blue	p-Nitrobenzoate	.5	.25	.2	.15	.1	.1	.1
Brom phenol blue	Benzoate	− .85	−1.05	−1.05	−1.1	−1.1	−1.1	−1.1
Brom cresol green	Benzoate	.4	0.15	0.05	0.05	0.05	0.05	
Brom cresol green	Acetate	.15	− .1	− .15	− .2	− .2	− .2	
Brom cresol green	Ammonium	.05	− .5	− .65				
Brom cresol purple	Benzoate	1.8	1.55	1.5	1.45			
Brom cresol purple	Veronalate	−1.05	−1.3	−1.4	−1.45	−1.45	−1.45	−1.4
Brom thymol blue	Veronalate	0.1	−0.05	−0.15	−0.2	−0.2	−0.2	−0.2
Phenol red	Veronalate	.45	.2	.25	.1	.1	.1	.1
Thymol blue	Veronalate	2.1	1.85	1.8	1.8	1.75		
Thymol blue	Trichloroacetate	−0.4	−0.4	−0.4	−0.4	−0.35	−0.3	− .025
Methyl orange	Trichloroacetate	−2.4	−2.4	−2.35	−2.35	−2.3	−2.2	
Methyl red	Benzoate	0.2	0.2	0.2	0.2	0.2	0.25	0.35
Methyl red	Trichloroacetate	−2.25	−2.1	−1.95	−1.85	−1.7	−1.4	
Methyl yellow	Trichloroacetate	−2.7	−2.5	−2.4	−2.3	−2.15	−1.8	−1.5
Neutral red	Salicylate	−0.5	−0.25	−0.05	0.1	0.35		
Thymolbenzein	Trichloroacetate	−2.5	−2.25	−2.1	−2.05	−1.95	−1.7	−1.5
Thymolbenzein	Veronalate	0.8	0.8	0.85	0.9	1.0		

TABLE II
IONIZATION CONSTANTS OF INDICATORS IN ETHANOL

Indicator	Buffer	pK_A	pK'	$pK_{I(EtOH)}$	$pK_{I(MeOH)}$	$pK_{I(H_2O)}$
Tropeoline 00	Hydrogen chloride			2.3	2.2	2.0
Brom phenol blue	Salicylate	8.7[a]	0.8	9.5	8.9	4.1
Brom phenol blue	o-Nitrobenzoate	8.6[b]	1.0	9.6		
Brom phenol blue	m-Nitrobenzoate	9.2[b]	0.4	9.6		
Brom phenol blue	p-Nitrobenzoate	9.1[b]	.5	9.6		
Brom phenol blue	Benzoate	10.25[a]	− .85	9.4		
Brom cresol green	Benzoate	10.25	.4	10.65	9.8	4.9
Brom cresol green	Acetate	10.6[a]	.15	10.75		
Brom cresol green	Ammonium	10.5[a]	.05	10.55		
Brom cresol purple	Benzoate	10.25	1.8	12.05	11.3	6.4
Brom thymol blue	Veronalate	13.1	0.1	13.2	12.4	7.3
Phenol red	Veronalate	13.1	.45	13.55	12.8	8.0
Thymol blue(1)	Trichloroacetate	5.8[a]	− .4	5.35	4.7	1.65
Thymol blue(2)	Veronalate	13.1	2.1	15.2	14.0	9.2
Methyl orange	Trichloroacetate	5.8	−2.4	3.4	3.8	3.45
Methyl red(1)	Trichloroacetate	5.8	−2.25	3.55	4.1	2.3
Methyl red(2)	Benzoate	10.25	0.2	10.45	9.2	5.0
Methyl yellow	Trichloroacetate	5.8	−2.25	3.55	3.4	3.25
Neutral red	Salicylate	8.7	−0.5	8.2	8.2	7.4
Thymolbenzein(1)	Trichloroacetate	5.8	−2.5	3.3	3.5	
Thymolbenzein(2)	Veronalate	13.1	0.8	13.9	13.15	

[a] Dissociation constant of acid has been obtained from I. M. Kolthoff, *J. Phys. Chem.*, **35**, 2732 (1931).   [b] Dissociation constant of acid has been obtained from H. Goldschmidt, *Z. physik. Chem.*, **99**, 116 (1921).

Results.—As an example, the data obtained in an investigation of brom cresol green in benzoate buffer are shown by the solid curve in Fig. 1. From the graph, a value of $pK' = 0.4$ is obtained. Knowing that, for benzoic acid, $pK_A = 10.25^2$, we find pK_1 of brom cresol green to be 10.65.

In Table I is given a summary of pK values of indicator-buffer systems at various ionic strengths, as well as the values at infinite dilution. The behavior of indicator-buffer systems is more clearly seen in Fig. 2, where it is found that the systems studied fall into a few well-defined groups.

Discussion

The behavior of acid–base indicators in ethanol is much the same as in methanol. At infinite dilutions, the curves approach the slope of 5.8, required by the Debye–Hückel limiting law. At higher salt concentrations, the ionic diameter and individual molecular characteristics bring about variations that can be expected.

The behavior of sulfonephthaleins in ethanol is in agreement with the extension of the concept of Bjerrum[4] as discussed in a previous paper.[1] This is indicated in Fig. 1, in which the system of brom cresol green in benzoate is compared in methanol and ethanol. Although the general shapes of the curves are the same, the ethanol curve is compressed toward the zero-concentration axis. In other words, the individual effects of the separate charges on a zwitterion become apparent at much lower salt concentrations than in methanol. As a result, although the limiting slope is greater in ethanol, the limiting value

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

of pK above the horizontal portion of the curve is about the same in the two solvents.

The same comparison seems applicable in cases of the other zwitterion indicators, i. e., thymolbenzein, thymol blue in trichloroacetate and methyl orange. The behaviors of the basic indicators, methyl yellow and neutral red, are in accord with present concepts. Methyl red behaves as if the intermediate form (Red II) is a true amino acid and not a zwitterion, in agreement with results found in methanol. In trichloroacetate, it behaves as a cation acid; in benzoate as an uncharged acid.

In Table II is given a summary of the true ionization constants of the indicators studied. These are calculated from the pK' values obtained in this study and accepted values of pK_A found in the literature. The pK_A of veronal was found to be 13.1, from a study of the brom cresol purple–veronalate system. For comparison, the values in methanol and water are also listed. The value for tropeoline 00 was determined in dilute hydrogen chloride.

Summary

1. A study has been made of the dissociation of acid–base indicators in ethanol, especial attention being paid to the effect of ionic strength.

2. Values of thermodynamic ionization constants of these indicators have been measured.

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The Conductance of Solutions of Organosubstituted Ammonium Chlorides in Liquid Hydrogen Sulfide

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I. Introduction

Organic ammonium salts were found to form conducting solutions in the liquid hydrides of phosphorus, sulfur, and the halogens by McIntosh and Steele,[3] and in the liquid hydrides of the halogens and sulfur by Steele, McIntosh and

Archibald.[4] Antony and Magri[5] have reported that solutions of tetramethylammonium iodide, in liquid hydrogen sulfide, conduct. Quam and Wilkinson[6] have reported the conductances of solutions of methylammonium, dimethylammonium, and triethylammonium chlorides at a number of different concentrations in liquid hydrogen sulfide. Their work shows distinctly the