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

The Distribution of Protons between Water and Other Solvents

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

In a study of acid–base indicator equilibria in methanol[1] buffer solutions, it was found that traces of water have a negligible effect upon the equilibrium of the system, unless the water reacts with the indicator itself.[2] In unbuffered solutions of strong acids in alcohols, traces of water have a pronounced effect upon the color equilibrium of an indicator since water is a much stronger base than the alcohols.

Qualitatively, the effect of the addition of water to alcoholic solutions of strong acids is comparable to the effect of ammonia added to aqueous solutions of strong acids. In the present paper, the effect of traces of water added to a dilute solution of a strong acid in an alcohol, ROH, has been studied quantitatively with the aid of a suitable acid–base indicator. In anhydrous alcoholic solution, the strong acid is assumed to be completely ionized into alcoxonium ions, ROH_2^+ and anions. Upon addition of traces of water, the protons distribute themselves between the alcohol and water molecules according to the equation

$$ROH + H_3O^+ \rightleftarrows ROH_2^+ + H_2O$$

The equilibrium of this reaction is given by

$$K_p = \frac{a_{ROH_2^+}a_{H_2O}}{a_{H_3O^+}}$$

At very small ionic strengths, the activity coefficients of the ROH_2^+ and H_3O^+ ions may be taken equal. When the concentration of the water is very small, the activity of the water may be written equal to the concentration. Hence, under the specified conditions we may write

$$K_p = \frac{c_{ROH_2^+}c_{H_2O}}{c_{H_3O^+}} \qquad (1)$$

The equilibrium between the acid and alkaline forms, I_a and I_b, of an indicator in alcoholic medium is given by the expression

$$\frac{a_{I_b}}{a_{I_a}} = \frac{K_I}{a_{ROH_2^+}}$$

or

$$r = \frac{c_{I_b}}{c_{I_a}} = \frac{K_I}{c_{ROH_2^+}}\,\frac{f_{I_a}}{f_{I_b}f_{ROH_2^+}} \qquad (2)$$

If c is the concentration of the strong acid in the alcohol and c_{H_2O} the concentration of the water added, we have

$$c_{H_3O^+} + c_{ROH_2^+} = c \qquad (3)$$

From this and equation (1), it is derived that in the water-containing alcoholic solution

$$c_{ROH_2^+} = \frac{K_pc}{c_{H_2O} + K_p} \qquad (4)$$

Introducing this expression in equation (2), we find that

$$r = \frac{c_{I_b}}{c_{I_a}} = \frac{K_I}{c}\left[\frac{c_{H_2O}}{K_p} + 1\right]\frac{f_{I_a}}{f_{I_b}f_{ROH_2^+}} \qquad (5)$$

If we use a simple indicator base, such as methyl yellow, I_a is a positively charged univalent ion. It has been shown[3] that in such a case f_{I_a} can be taken equal to $f_{ROH_2^+}$ at small ionic strengths. Since I_{I_b} is a neutral molecule we then have, instead of (5)

$$r = \frac{c_{I_b}}{c_{I_a}} = \frac{K_I}{c}\left[\frac{c_{H_2O}}{K_p} + 1\right] \qquad (6)$$

By plotting values of the indicator color ratio, r, against water concentration, the intercept is K_I/c and the slope, K_I/cK_p, leads to the evaluation of K_p. Since $C_{H_3O^+}$ is negligible, compared with C_{H_2O}, the latter may be taken equal to the concentration of water added.

By studying the change in conductivity of hydrochloric acid solutions on the addition of traces of water, Goldschmidt and co-workers obtained the values of K_p of 0.0583 in ethanol[4] and of 0.235 in methanol.[5] These values are substantiated in this investigation and the method is extended to the solvent *n*-butanol.

Materials.—Methanol and ethanol were purified by methods already described,[1,6] the final product having less than 0.01% of water as estimated from density measurements. *n*-Butanol was dehydrated with aluminum amalgam[7] and distilled from anhydrous copper sulfate. Its density ($d^{25}{}_4$) measured with a 100 ml. pycnometer was found to be 0.80579. Methyl yellow was recrystallized from a water–methanol solution.

Dry hydrogen chloride was prepared by dropping concentrated sulfuric acid into concentrated hydrochloric acid, passing the gas through a wash bottle of concentrated sulfuric acid, then through a plug of glass wool. It was

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[1] I. M. Kolthoff and L. S. Guss, THIS JOURNAL, **60**, 2516 (1938).

[2] I. M. Kolthoff and L. S. Guss, *ibid.*, **61**, 16 (1939).

[3] I. M. Kolthoff and L. S. Guss, *ibid.*, **61**, 330 (1939).

[4] H. Goldschmidt, *Z. physik. Chem.*, **89**, 129 (1914).

[5] H. Goldschmidt and P. Dahll, *ibid.*, **108**, 121 (1924).

[6] L. S. Guss and I. M. Kolthoff, THIS JOURNAL, **62**, 249 (1940).

[7] P. Walden, H. Ulich and F. Laun, *Z. physik. Chem.*, **114**, 275 (1925).

finally washed in the solvent to be used. Such solutions were prepared immediately before use to diminish errors due to esterification. Standard solutions of water were prepared as previously described.[2]

Method.—A measured volume of hydrogen chloride was introduced into a test-tube, 0.5 ml. of methyl yellow solution (0.0001 *M*) added and the volume made up to 5.0 ml. with the pure solvent. The ratio r was measured by the Gillespie method. The procedure was then repeated with the same solution containing known concentrations of water. These data are listed in Tables I, II and III.

TABLE I

EFFECT OF WATER ON METHYL YELLOW IN METHANOL

	r		
c_{H_2O}	$c_{HCl} = 0.00080$	$c_{HCl} = 0.00107$	$c_{HCl} = 0.00160$
0	0.67	0.47	0.33
0.12	.905	.67	.43
.24	1.22	.92	.67
.36	1.50	1.13	.82
.48	1.70	1.44	.89
.60	2.33	1.78	1.22
Intercept	0.63	0.42	0.32
Slope	2.44	2.16	1.36
K_p	0.258	0.194	0.235

TABLE II

EFFECT OF WATER ON METHYL YELLOW IN ETHANOL

	r		
c_{H_2O}	$c_{HCl} = 0.0016$	$c_{HCl} = 0.0024$	$c_{HCl} = 0.032$
0	0.54	0.33	0.25
0.02	.75	.43	.30
.04	.89	.54	.37
.06	1.13	.67	.47
.10	1.50	.89	.59
.16	2.03	1.22	.89
Intercept	0.58	0.326	.225
Slope	9.4	5.6	4.0
K_p	0.062	0.058	0.056

TABLE III

EFFECT OF WATER ON METHYL YELLOW IN BUTANOL

	r		
c_{H_2O}	$c_{HCl} = 0.00118$	$c_{HCl} = 0.00178$	$c_{HCl} = 0.00236$
0	0.67	0.47	0.37
0.02	1.13	0.72	.59
.04	1.63	1.00	.67
.06	2.33	1.38	.82
.08	2.57	1.50	1.04
.10	3.0	1.63	1.38
.12			1.50
.14		2.33	
.16			1.86
Intercept	0.70	0.48	0.32
Slope	23.8	12.8	9.8
K_p	0.029	0.038	0.033

Values of r were plotted against c_{H_2O} and from the curves K_p was evaluated. As an example, the data obtained in methanol are plotted in Fig. 1. For the sake of brevity, the figures referring to the data in ethanol and *n*-butanol are omitted. All determinations were carried out in the temperature range 25 ± 2°.

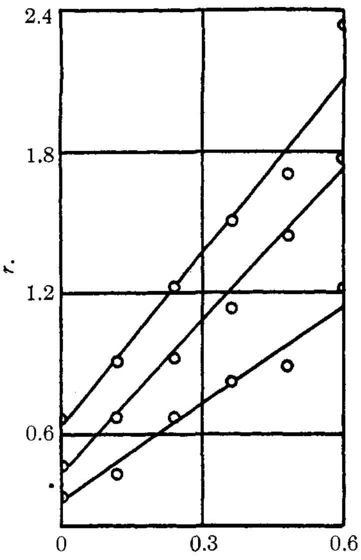

Fig. 1.—Effect of water on methyl yellow in methanol.

Discussion

The average values of K_p obtained by these measurements are 0.23, 0.059 and 0.033 for methanol, ethanol, and butanol, respectively. The first two are in agreement with the values obtained by Goldschmidt of 0.235 and 0.0583. While ethanol is a much weaker base than methanol, *n*-butanol is not much less basic than ethanol.

The fact that all points fall fairly well on straight lines substantiates the validity of the derivation in the introduction. There might, however, be a doubt in the assumption that hydrogen chloride is completely dissociated in such solvents of low dielectric constant. If we take this into consideration, equation 3 would become

$$c = c_{H_3O^+} + c_{ROH_2^+} + c_{HCl} = c_{ROH_2^+}\left[\frac{c_{H_2O}}{K_p} + 1 + \frac{c_{Cl^-}}{K_{HCl}}\right]$$

where K_{HCl} is the dissociation constant of hydrogen chloride. Equation 6 then becomes

$$r = \frac{K_1}{c}\left[\frac{c_{H_2O}}{K_p} + 1 + \frac{c_{Cl^-}}{K_{HCl}}\right]$$

Hence, if the acid were not completely dissociated, we would expect an increase in K_p with an increase in acid concentration. Since the values of K_p check within experimental error in all three cases, our assumption of complete dissociation is valid.

The results of the experiments give us a method of evaluating the dissociation constant of methyl yellow in these solvents. In Table IV are listed these values, along with values obtained by other methods.

TABLE IV

DISSOCIATION CONSTANT OF METHYL YELLOW

Solvent	pK_I	pK_I (lit.)
Methanol	3.3	3.4[1]
Ethanol	3.1	3.1[a]
Butanol	3.1	2.8[b]

[a] The value reported by us in a previous paper (ref. 5) was erroneously given as 3.55 instead of 3.1. [b] R. B. Mason and M. Kilpatrick, THIS JOURNAL, **59**, 372 (1937).

There is a satisfactory check in the case of methanol and ethanol. The lack of agreement in butanol might be due to the presence of water in the butanol used by Mason and Kilpatrick. The amount of water can be estimated from these data. From equation (6) we find

$$K_I' = K_I\left[\frac{c_{H_2O}}{K_p} + 1\right]$$

where K_I' is the apparent dissociation constant. So

$$pK_I - pK_I' = \log\left(\frac{c_{H_2O}}{K_p} + 1\right)$$

Setting $pK_I - pK_I' = 0.3$, and $K_p = 0.033$, we get $c_{H_2O} = 0.033$ mole per liter, corresponding to 0.075% water in the butanol used by the above authors.

The colorimetric method could be used for the determination of traces of water in ethanol and butanol. From equation (6) it follows that

$$c_{H_2O} = K_p\left(\frac{rc}{K_I} - 1\right)$$

It is seen from Table II that the ratio r increases about 2.5 times when 0.18% water is added to pure ethanol.

Summary

1. The effect of traces of water on the color equilibrium of methyl yellow in dilute solutions of hydrogen chloride in methanol, ethanol and butanol, has been studied.

2. The relative basicities of these solvents have been determined and were found to decrease in the order: methanol, ethanol, butanol.

3. The dissociation constant of methyl yellow in these solvents has been calculated.

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The Change with Time of the Surface Tension of Solutions of Sodium Cetyl Sulfate and Sodium Lauryl Sulfate

BY G. C. NUTTING, F. A. LONG AND WILLIAM D. HARKINS

Introduction

The static value of the surface tension of a pure liquid is attained within a very minute time after the surface is formed, for in order to reduce the surface free energy to its minimum value only a reorientation of molecules already present is necessary. With solutions, however, there is in general at equilibrium an excess or deficiency of solute in the surface layer and an appreciable time interval may be required for the transport of solute molecules from the bulk of the solution into the surface or *vice versa*.

Bond and Puls[1] have measured the surface tension of surfaces whose age is about 0.003 sec. and find that for a variety of aqueous solutions, including solutions of inorganic salts and the lower aliphatic alcohols, the surface tension even in so short a time changes to approximately the static value. They have been able to show that their experimental values of the surface tension change agree reasonably well with predicted values if diffusion alone is responsible for the time effect.

In the case of certain other solutions the final surface tension is not reached until days or weeks have passed. Examples are solutions of paraffin chain salts and of other molecules which are in part strongly hydrophobic, yet which dissociate into ions in water.[2] Doss[3] has presented evidence that unhindered diffusion would lead to establishment of equilibrium in the surface in a far shorter time than is observed, and that the rate of diffusion of the ions is slowed up enormously near the surface by the electrostatic repulsion of the ions already present in the surface layer.

In the present paper data are presented on the change with time of the surface tension of solutions of sodium cetyl sulfate and sodium lauryl

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[1] W. N. Bond and H. O. Puls, *Phil. Mag.*, **24**, 864 (1937).

[2] N. K. Adam and H. L. Shute, *Trans. Faraday Soc.*, **34**, 758 (1938).

[3] K. S. G. Doss, *Kolloid-Z.*, **86**, 205 (1939).