in l./mole-sec. at 25° for the hydrochloric acid catalyzed hydrolysis in 70% aqueous acetone are for methyl acetate 5.45,[2b] for ethyl acetate 4.64,[2b] for ethyl propionate 3.95.[4b] In contrast to this 28% decrease, the rates in water increase by 13% from methyl acetate to ethyl propionate (*cf.* Table I). For the esters of lower molecular weight the effect in alcohol–water solvent appears to arise chiefly or entirely from a decrease in entropy of activation with increasing chain length.[4a] It is therefore of a kind which may be attributed to a hampering of the internal motions of the ester molecule when it is converted to the transition state for the hydrolysis with a resultant decrease in entropy which parallels the entropy of the reactant ester.[6] We would suggest that all the effects here considered are consistent with the following hypothesis. In the mixed solvents the electrically charged transition state is subjected to restraints arising from solvation, which are stronger than those acting on the ester. These lead to a decrease in entropy of activation which is greater the greater the chain length of the ester. Still greater restraints imposed by the resin network lead to still greater decreases in entropy of activation with increasing chain length in the resin-catalyzed reaction. In water solution, however, the solvation of the polar groups in the ester itself is so powerful that no further important restraints are imposed on the internal motions of the ester by the solvation of the charged transition state or by the resin network (except in the most highly cross linked resins). Consequently the entropy change involved in the conversion of ester to transition state is no longer more negative for esters of greater chain length.

We wish to acknowledge the help of Mr. Eugene Garfield, who assisted with many of the measurements and calculations.

Experimental

The experimental methods were those described previously.[2b] All runs were made at least in duplicate, those used in the temperature coefficient studies being in triplicate. Agreement was better than 1% in all cases except those involving ethyl propionate. Plus and minus values for the energies of activation listed in Table II refer to mean deviations between high and low temperature range calculations, except when these agreed to better than 200 cal. In such cases a minimum error of 200 cal. was assumed, this being the value arising from the estimated probable error in the specific rates derived from least squares analysis of concentration–time plots.

Commercial Dowex-50 was purified by the methods of Gregor and associates,[7] and 45–50 mesh particles were used in the rate measurements. The other resins have been described previously.[2]

---

[6] F. P. Price and L. P. Hammett, THIS JOURNAL, **63**, 2387 (1941).

[7] H. P. Gregor, J. I. Bregmann, F. Gutoff, R. D. Breadley, D. E. Baldwin and C. G. Overberger, *J. Colloid Sci.*, **6**, 20 (1951).

NEW YORK, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Acid–Base Levels in Methanol–Water and 1,4-Dioxane–Water Solutions

BY W. C. WOODLAND,[1] ROBERT B. CARLIN AND J. C. WARNER

RECEIVED MARCH 12, 1953

The apparent acid–base levels of 3.077×10^{-3} *M* sodium hydroxide solutions in methanol–water and dioxane–water have been studied at approximately 25° by means of an indicator method. Complete absorption spectra were determined for both acid and base forms of Alizarin Yellow R in the range 220–600 mμ in water, in methanol and in methanol–water and dioxane–water solutions of various compositions; and extinction coefficients were determined at 375 and 495 mμ in the various solvents both for the acid and for the base forms of the indicator. A knowledge of these values allowed analyses to be made for the concentrations of the base and of the acid form, and thence the "indicator ratio," R = [base form]/[acid form], in any of the solvents or solvent combinations. Values for R were determined in water solutions in which there was a constant concentration of sodium hydroxide but in which the ionic strength was varied by adding potassium chloride. Extrapolation of the log R values to zero ionic strength gave a limiting ratio from which pK for the Alizarin Yellow R indicator was calculated to be 11.17. The slope of the log R *vs.* $\sqrt{\mu}$ curves at low ionic strengths supported the assumption that the indicator base is a doubly charged anion and the acid a singly charged anion. Similar log R extrapolations to zero ionic strength were made for 3.077×10^{-3} *M* solutions of sodium hydroxide in methanol–water and in dioxane–water. The relative order of these limiting log R values was shown to be the same as that of the p_aH values, and the experimental observations indicated that sodium hydroxide solutions in methanol–water have lower p_aH values than isodielectric dioxane–water solutions of the same sodium hydroxide concentration. Apparent p_aH values for these solutions were calculated from the indicator pK, the limiting log R values, and activity coefficient ratios computed by assuming 2 and 3 Å. indicator ion radii. These calculations showed that p_aH increases with decreasing dielectric constant in dioxane–water solutions, but that methanol–water solutions show the opposite behavior. The dielectric constant effect in dioxane–water solutions is normal; therefore the base levelling effect in methanol–water gives rise to the postulate that methanol is a stronger acid than water.

A critical evaluation of all previous investigations directed toward a comparison of the acid–base properties of water with those of the lower aliphatic alcohols and toward determining the extent to which hydroxyl ion is levelled by methanol has led us to the following conclusion: Although a recent investigation[2] has provided quantitative evidence indicating that methanol is a stronger acid than water in isopropyl alcohol solution, and although there are many other lines of evidence which indicate that methanol is a stronger acid than water, no unambiguous quantitative results are available for methanol–water solutions. In the study described in this paper, evidence bearing on the question of the comparative acid strengths of methanol and water was provided by determining the apparent hydrogen ion activities in methanol–water and in 1,4-dioxane–water solutions containing identical concen-

---

[1] Abstracted from a thesis submitted by W. C. Woodland to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the D.Sc. degree.

[2] J. Hine and M. Hine, THIS JOURNAL, **74**, 5266 (1952).

trations of added base. The experimental method was based on the use of an indicator, the concentrations of the acid and base forms of which were measured spectrophotometrically.

Experimental

Nitrogen employed throughout this work was dried and freed of carbon dioxide.

All water solutions were made with distilled water which had been boiled under reduced pressure and stored under nitrogen. Standard aqueous and methanolic alkalies were freed of carbonates and stored under nitrogen. In general, solutions were prepared and transferred in carbon dioxide-free atmosphere. The cell cavity of the Beckman spectrophotometer was provided with a light-tight cover fitted with an air inlet which extended to the bottom of the cavity. Dry, carbon dioxide-free air was introduced through the inlet into the cell compartment while spectral measurements were being made on very weakly basic solutions. Such solutions did not absorb detectable amounts of carbon dioxide under these conditions.

Methanol employed in this work was obtained by distilling reagent grade anhydrous methanol through an 18-inch glass-helix-packed column. The "middle cut" boiling over a 0.1° range was selected for use. **Sodium methoxide** solutions were prepared by dissolving sodium in methanol.

1,4-Dioxane was purified by means of the procedure recommended by Weissberger and Proskauer.[3]

Potassium chloride (Fisher Scientific Co., C.P.) was recrystallized twice from distilled water, dried for three hours at 220° and powdered in an agate mortar in order to facilitate its dissolution in organic solvents.

Alizarin Yellow R was precipitated by adding hydrochloric acid to an aqueous solution of the commercial sodium salt (Fisher Scientific Co.). After two recrystallizations from aqueous acetic acid, it had the m.p. 255° dec. The m.p. 253–254° dec. has been reported.[4]

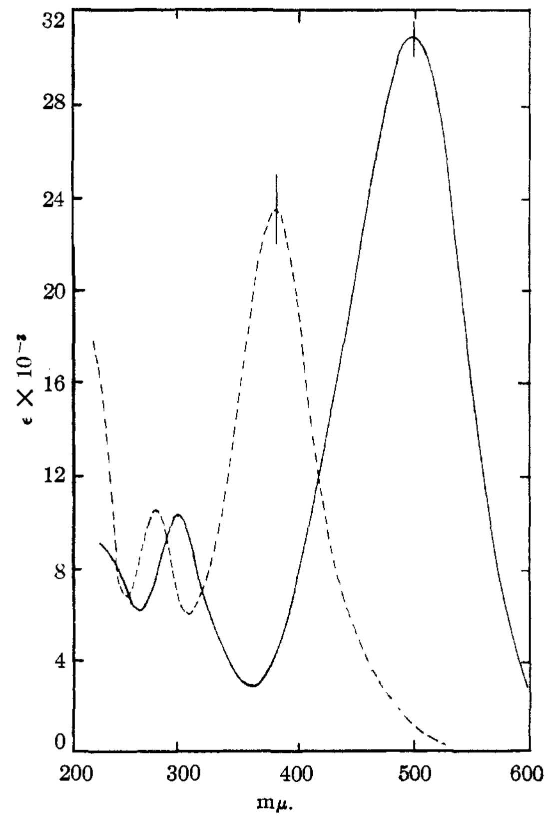


Fig. 1.—Extinction curves for the acid form (- - - - -) and for the base form (————) of Alizarin Yellow R in water solution.

Anal. Calcd. for $C_{13}H_9O_5N_3$: C, 54.4; H, 3.17; N, 14.63. Found: C, 54.4; H, 3.26; N, 14.72.

Measurements of Extinction Coefficients.—Solutions of the base form of the indicator were prepared by dissolving the crystalline indicator acid (weighed on a micro-balance) in the appropriate solvents containing excess alkali. Solutions of the acid form in all solvents except water were made by dissolving the crystalline indicator acid in methanol or dioxane and diluting with water to form solutions in the mixed solvents. The low rate of solution of the indicator acid in water made it expedient to dissolve the former in aqueous sodium hydroxide and then to add at least sufficient standard hydrochloric acid to neutralize the base. Indicator molarities in these solutions ranged up to 3.7×10^{-5}.

A Beckman quartz spectrophotometer, model DU, was used to measure optical densities and extinction coefficients. Optical densities of indicator solutions were generally determined from ratios of absorptions in calibrated quartz cells of pairs of solutions which were identical except for the absence of indicator in one member of each pair. Although the temperature within the cell cavity of the instrument could not be controlled thermostatically, an effort was made to keep solutions within the range 25–30° upon introduction into the instrument and to take readings quickly enough so that substantial temperature changes were avoided.

The extinction curves for the acid and base forms of the indicator in water solution have maxima at 375 and 495 mμ, respectively (Fig. 1), and a minimum for each curve occurs in the region where a maximum is found in the other. Therefore, indicator analyses were based upon optical density measurements at 375 and 495 mμ. Although slight shifts in the positions of the maxima were observed when dioxane or methanol replaced part or all of the water as solvent, these shifts were not great enough to require that new wave lengths be chosen for analysis. Both forms of the indicator obeyed Beer's law in all solutions except those of the base form in methanol (and, of course, in dioxane, in which the base form is insoluble). Apparently the indicator is not completely converted to its base form in pure methanol even at sodium methoxide concentrations greater than 0.8 *M*. Molar extinction coefficients for the acid and base forms of Alizarin Yellow R at 375 and 495 mμ were obtained from the slopes of the Beer's law plots (optical density *vs.* concentration) and are shown in Table I.

Table I

Molar Extinction Coefficients of Alizarin Yellow R in 1,4-Dioxane–Water and Methanol–Water Mixtures

	Molar extinction coefficient (ϵ) $\times 10^{-4}$			
	Acid form		Base form	
Dioxane, %	375 mμ	495 mμ	375 mμ	495 mμ
0.0	2.360	0.149	0.405	3.110
10.21			.351	3.141
20.12	2.377	.175		
25.24			.310	3.177
35.0	2.350	.194		
40.04	2.291	.214		
49.90			.276	3.131
50.00	2.330	.206		
100	2.505	.0775		
Methanol, %				
7.8			.386	3.161
20.49	2.443	.143		
42.58	2.486	.156		
47.4			.325	3.159
100	2.500	.130		

Determination of "Indicator Ratio."—From data of Table I smooth curves were drawn to represent the relationship between solvent compositions and molar extinction coefficients for the acid and base forms at each of the two wave lengths. These relationships were not linear. From the curves, extinction coefficients could be computed for solvent mixtures having compositions intermediate among those from which the calibration curves were drawn.

---

[3] A. Weissberger and E. S. Proskauer, "Organic Solvents," Oxford University Press, New York, N. Y., 1935, p. 135.

[4] J. T. Hewitt and J. J. Fox, *J. Chem. Soc.*, **79**, 49 (1901).

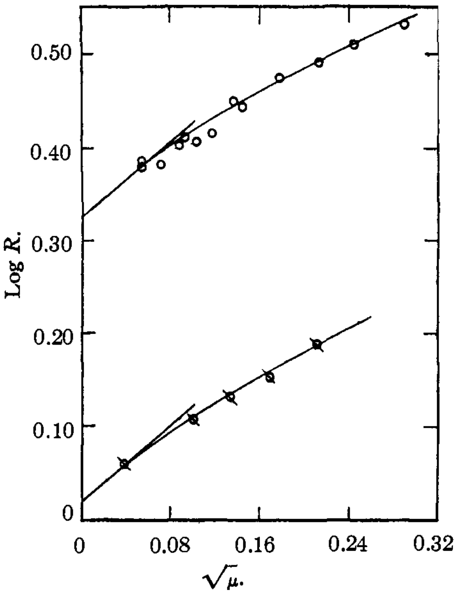


Fig. 2.—Dependency of indicator ratio (R) on ionic strength (μ) in water solutions 3.077×10^{-3} M (○) and 1.539×10^{-3} M (⊖) in sodium hydroxide.

From the equation

$$D_{375} = \epsilon_{375}[B] + \epsilon_{375}[A]$$

(where D is optical density, A and B refer to acid and base forms, respectively, 375 refers to measurements made at 375 mμ, and the ε values are known for the solvent composition being investigated) and an analogous equation for measurements made at 495 mμ, [A] and [B] could be calculated, after D readings were taken for any unknown indicator solution at 375 and at 495 mμ. The sum [A] + [B] from concentrations determined in this way always agreed well with the known total indicator concentration. In the work to be described later, the "indicator ratio," defined as R = [B]/[A], rather than the individual concentrations, is the function required. Determinations of R in solutions of varying ionic strength were carried out by measuring indicator ratios in series of solutions; in each series the only variable component was potassium chloride. For each series a master solution was prepared which contained measured quantities of indicator, of alkali and of solvent. Portions of this solution were then transferred to a series of 50-ml. volumetric flasks containing varying weighed amounts of potassium chloride. The quantity R was then determined for each solution in the series. Log R was plotted against the square root of the ionic strength (μ), and an extrapolation to zero ionic strength was made, using as a guide the theoretical slope at zero ionic strength derived from the Debye-Hückel theory. Figure 2 shows two such plots of data obtained from water solutions; the two sets of solutions from which the respective curves are derived differed in constant alkali concentration. In Fig. 3 are shown similar plots for mixed solvents. The sodium hydroxide concentration was 3.077×10^{-3} M in all these solutions. Table II shows the dielectric constants and values of log $R_{\mu = 0}$ for ten solvent combinations.

TABLE II

Dioxane, %	D^a	Log $R_{\mu\to 0}$	Curve, fig. 3	Theoretical slope
0.00	78.48	0.325	..	1.01
10.36	70	.09	I	1.20
21.10	59.9	− .17	II	1.51
31.06	51.3	− .395	III	1.93
36.1	47.0	− .47	IV	2.22
41.6	41.6	− .61	V	2.62
Methanol, %				
19.74	68.4	− .30	VI	1.23
34.56	61.4	− .76	VII	1.42
40.76	58.2	− .95	VIII	1.56
53.4	52.6	−1.131	IX	1.83

[a] D values for 1,4-dioxane-water mixtures were taken from the work of G. Akerlof and O. A. Short, THIS JOURNAL, **58**, 1251 (1936); for methanol-water mixtures, D-values were taken from the work of P. S. Albright and L. J. Gosting, *ibid.*, **68**, 1061 (1946).

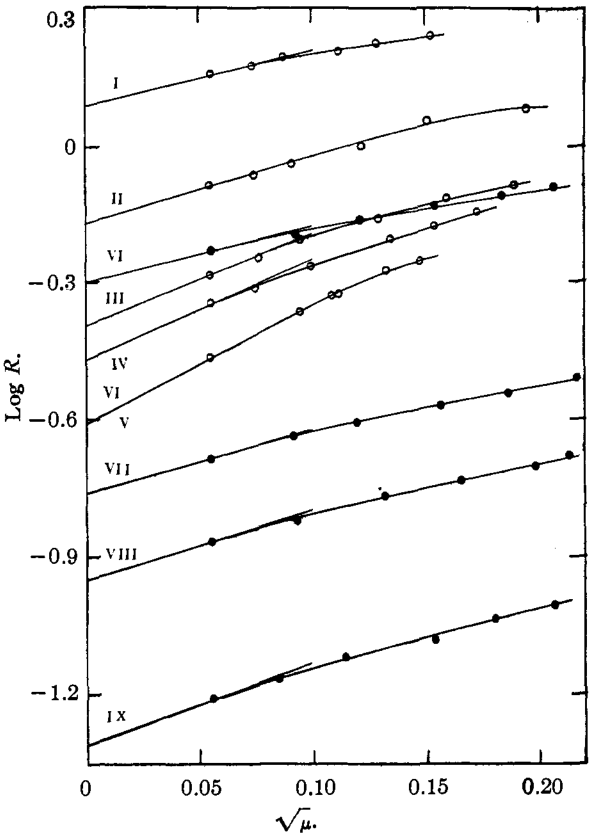
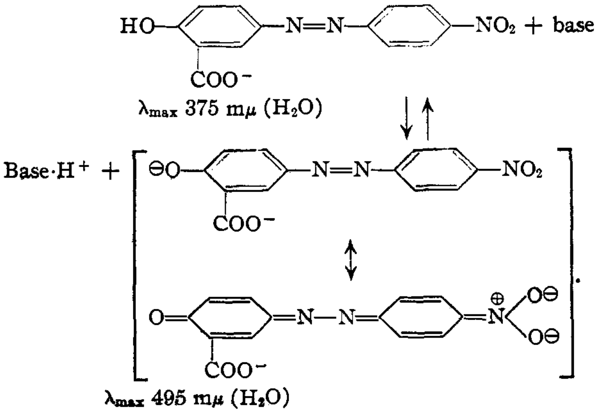


Fig. 3.—Dependency of indicator ratio (R) on ionic strength (μ) in dioxane-water (○) and in methanol-water (●) solutions 3.077×10^{-3} M in sodium hydroxide.

Results and Discussion

Determination of *pK* for Alizarin Yellow R.—There can be little doubt that the indicator color change of Alizarin Yellow R is the result of the following transformation



The acid form therefore bears a single negative ionic charge; the base form a double negative one.

The thermodynamic indicator constant is therefore

$$K = a_{H^+} \times a_{In^=}/a_{HIn^-}$$

which leads to

$$pK = p_aH - \log R - \log(\gamma^{=}/\gamma^{-}) \qquad (1)$$

(where the γ's are activity coefficients of the indicator ions, with infinite dilution in water as the reference state). In water solution

$$p_aH = pK_w + \log[OH^-] + \log\gamma^- \qquad (2)$$

Combining 1 and 2

$$pK = pK_w + \log[OH^-] - \log R - \log[\gamma^{=}/(\gamma^-)^2] \qquad (3)$$

For a series of water solutions in which $[OH^-]$ is constant, 3 becomes

$$\log R = \text{const.} - \log[\gamma^{=}/(\gamma^-)^2] \qquad (4)$$

From Debye–Hückel theory 4 reduces to

$$\log R = \text{const.} + 1.01\sqrt{\mu}\ (\text{at } 25°)$$

The fact that log R *vs.* $\sqrt{\mu}$ plots (Fig. 2) extrapolate satisfactorily to unit slopes at zero ionic strength and that plots of the same functions in other solvents extrapolate to slopes agreeing similarly (Fig. 3) with those computed from Debye–Hückel theory constitutes support of the assumptions concerning the charge-types of the indicator acid and base.

As infinite dilution in water is approached, $\log[\gamma^{=}/(\gamma^-)^2]$ approaches zero, and equation 3 becomes

$$pK = pK_w + \log[OH^-] - \log R_{\mu=0} \qquad (5)$$

By means of equation 5 and the two values (Fig. 2) for log $R_{\mu=0}$ of 0.325 and 0.020 when $[OH^-] = 3.077 \times 10^{-3}$ and 1.539×10^{-3}, respectively, pK is computed as 11.166 and 11.171, respectively. The average, 11.17, may be compared with 11.2 reported by Kolthoff.[5] Given values of log $R_{\mu=0}$ in mixed solvents of varying dielectric constant, an assessment of an apparent p_aH for each solution may be made from the relation

$$p_aH = pK + \log R_{\mu=0} + \log\gamma^{=}/\gamma^- \qquad (1a)$$

provided that an evaluation of the activity coefficient ratios at infinite dilution in the various solvents may be accomplished. An approximation of this ratio may be computed by making use of a relationship derived by Laidler and Eyring,[6] which expresses the activity coefficient of an ion in a condensed medium relative to the ion in the gas state

$$\log f^s = \frac{z^2\epsilon^2}{4.606\,rkT}\left(\frac{1}{\mathbf{D}} - 1\right) - \frac{z^2\epsilon^2}{4.606\,Dkt}\,\frac{K}{1 + aK} + b\mu + \frac{\phi}{kT} \qquad (6)$$

where the first term arises from the work done in bringing the ion into a medium of dielectric constant **D**, the second and third terms represent the Debye–Hückel contribution to the free energy of transfer, and the fourth represents an all-inclusive non-electrostatic term composed, in part at least, of dispersive forces. For our work at $\mu = 0$, equation 6 becomes

$$\log f^s = \frac{z^2\epsilon^2}{4.606\,rkT}\left(\frac{1}{\mathbf{D}} - 1\right) + \frac{\phi}{kT}$$

where z is the valence, ϵ the electronic charge and r the ionic radius. Subtraction of this equation for water from that for a mixed solvent of dielectric constant $\mathbf{D}_x$, leads to

$$\log\gamma^s = \frac{z^2\epsilon^2}{4.606\,rkT}\left(\frac{1}{\mathbf{D}x} - \frac{1}{\mathbf{D}_{H_2O}}\right) + \frac{\phi_x - \phi_{H_2O}}{kT}$$

where γ^s now represents the activity coefficient of an ion at infinite dilution in the mixed solvent relative to infinite dilution in water. For purposes of calculation, we have set the difference in non-electrostatic contributions equal to zero. The neglect of the ϕ terms in the calculation of the activity coefficients probably does not lead to large errors since, for an ion, electrostatic contributions to the free energy of transfer doubtless are much greater than non-electrostatic contributions. Our activity coefficient term thus becomes

$$\log\frac{\gamma^{=}}{\gamma^{-}} = \frac{3\epsilon^2}{4.606\,rkT}\left(\frac{1}{\mathbf{D}x} - \frac{1}{\mathbf{D}_{H_2O}}\right) \qquad (7)$$

Equation 7 shows that the activity coefficient ratio of equation 1a at a given temperature and for a given indicator is mainly a function of the dielectric constant of the solvent. Therefore, the activity coefficient ratios should be nearly identical for two infinitely dilute solutions in different solvent mixtures of the same dielectric constant, and the comparative acidity levels of such solutions should be measured directly by the comparative values of log $R_{\mu=0}$, in accordance with equation 1a. Figure 4 shows that log $R_{\mu=0}$ (Table II) for sodium hydroxide solutions in methanol-water is always substantially less than the value of this function in dioxane–water solutions containing the same concentration of sodium hydroxide and having the same dielectric constant. Thus the acid level is higher (and the base level lower) for methanol–water solutions containing a fixed concentration of sodium hydroxide than for isodielectric constant dioxane–water solutions.

Since pK is known and log $R_{\mu=0}$ values for solutions of fixed sodium hydroxide concentrations in methanol–water or dioxane–water of a given dielectric constant can be obtained from Fig. 4, a p_aH value for any such solution can be computed (equation 1a) if $\log(\gamma^{=}/\gamma^-)$ can be evaluated. Equation 7 permits an evaluation of this function only if the ionic radius (r) of the indicator is known. Although no such value is recorded for Alizarin Yellow R, it probably lies between 2 and 3 Å. Amis and LaMer[7] have reported an ionic radius of 2.6 Å. for brom phenol blue, an indicator of the same charge type as Alizarin Yellow R and probably of comparable size. Accordingly, $\log(\gamma^{=}/\gamma^-)$ has been calculated from equation 7 for solutions of various dielectric constants, using both 2 and 3 Å. as values for r, and the resulting quantities have been substituted into equation 1a. A series of p_aH values as a function of dielectric constant was thereby derived for methanol–water and for dioxane–water solutions. Examination of these curves shows that p_aH for dioxane–water solutions probably increases continuously with decreasing dielectric constant, but a decrease in p_aH with decreasing dielectric constant is found in methanol–water solu-

---

[5] I. M. Kolthoff, "Acid–Base Indicators," The Macmillan Co., New York, N. Y., 1937, p. 148.

[6] K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **64**, 2065 (1942).

[7] E. S. Amis and V. K. LaMer, THIS JOURNAL, **61**, 905 (1939).

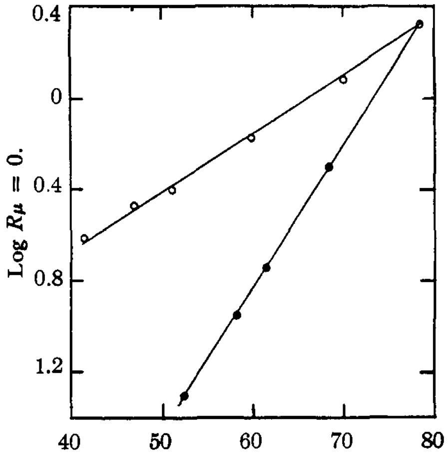


Fig. 4.—Log $R_{\mu=0}$ *vs.* dielectric constant for dioxane-water (O) and methanol-water (●) solutions 3.077 × 10^{-3} *M* in sodium hydroxide.

tions, all of which contain a fixed concentration of sodium hydroxide. Inasmuch as dioxane cannot react chemically with a base, it is reasonable to assume that the observed p_aH behavior of dioxane-water solutions (Fig. 5) is mainly an effect of the dielectric constant itself. The methanol-water solutions, however, show the opposite trend (Fig. 5); a base-leveling effect occurs as the methanol proportion increases. This behavior can be interpreted in terms of the equilibrium process

$$OH^- + CH_3OH \rightleftarrows CH_3O^- + H_2O$$

If methanol is a stronger acid than water then, as the methanol proportion increases, the concentration of the more weakly basic methoxide ion will increase at the expense of the more strongly basic hydroxide ion, and the base strength of the solution will decline.

An increasing downward deflection of the dioxane-water curves of Fig. 5 with decreasing dielectric constant would be necessary if corrections are made in the activity coefficient term of equation 1a in accordance with a hypothesis advanced by Laidler and Eyring.[6] If the effective dielectric constant is greater than the macroscopic value because of a tendency of ions to "sort out" water molecules from the mixed solvent, then the log $(\gamma^{=}/\gamma^{-})$ terms calculated by means of equation 7, using the macroscopic dielectric constants, are greater than they should be, and the increment of error increases with decreasing dielectric constant. These increments of error will then be passed on to the p_aH values. However, in view of the fact that the mole fraction of dioxane in the dioxane-water solutions is never greater than 0.13, any error incurred by failure to consider the "sorting out" effect cannot be great. The existence of such an effect in methanol-water solutions is subject to serious doubt. In any event, the qualitative trends of the curves of Fig. 5 and the conclusion that methanol levels the basicity of sodium hydroxide solution should not be affected.

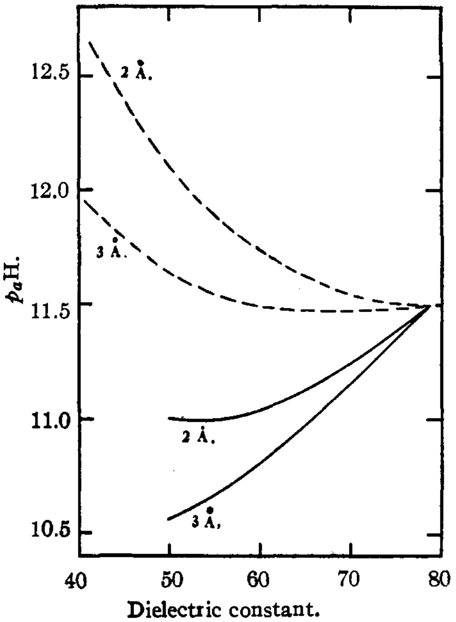


Fig. 5.—Plots of p_aH *vs.* dielectric constant for dioxane-water (- - - - -) and methanol-water (————) solutions 3.077 × 10^{-3} *M* in sodium hydroxide, assuming 2 and 3 Å. radius for the Alizarin Yellow R ion.

PITTSBURGH PENNA.