

Fig. 3.—The electron paramagnetic resonance (derivative) spectrum of polycrystalline silver phthalocyanine at room temperature.

$d_{x^2-y^2}$ is a silver 4d-atomic orbital. Overlap is included in the B_{1g} -orbital and related to the coefficients α and α' , by $\alpha' = \frac{1}{2}\alpha S + \sqrt{1 - \alpha^2}$, where S is taken to be 0.1. The spin Hamiltonian of an electron in a tetragonal electric field can be written as

$$\mathcal{H}_s = g_{\parallel}\beta_e(H_z S_z) + g_{\perp}\beta_e(H_y S_y + H_x S_x) + A(S_z I_z^{A\kappa}) + B(S_y I_y^{A\kappa} + S_x I_x^{A\kappa}) + C(S_z I_z^N) + D(S_y I_y^N + S_x I_x^N)$$

The parameter $b' = \frac{1}{3}(2D + C)$, is related to the molecular orbital coefficient α' by

$$(\alpha')^2 = \frac{9b'hc}{4\pi\gamma_N\beta_e\beta_N|\rho_N(0)|^2}$$

where $\gamma_N = 0.4037$ and $|\rho_N(0)|^2 = 33.4 \times 10^{24} \text{ cm.}^{-3}$.

The best values for the resonances corresponding to H_{\perp} and H_{\parallel} (Fig. 2) are given by:

$$H_{\perp}(\text{gauss}) = 3238.7 - 33.9m_1 - 24.6m_2$$

$$H_{\parallel}(\text{gauss}) = 3120.0 - 75.1m_1 - 21.9m_2$$

which correspond closely to the spectrum of silver(II) porphyrin.⁴ The Ag nuclear spin, $\pm 1/2$, is m_1 , and $m_2 = \pm 4, 3, \dots, 0$, the total N^{14} nuclear spin.

The results are compared to those for copper phthalocyanine and silver porphyrin in Table I.

From the paramagnetic resonance spectrum of polycrystalline silver phthalocyanine (Fig. 3), the value of g_{\perp} could be determined by the method of Kneubühl¹² and was found to be 2.016 (± 0.001), in close agreement with that for the frozen solution.

Although the B_{1g} -molecular orbital is covalent, for the odd electron can be found in the silver $d_{x^2-y^2}$ orbital about 54% of the time, silver phthalocyanine, in contrast to copper phthalocyanine, is readily demetallized by strong acids. This has been attributed in general to the labile covalent metallophthalocyanines because of the unfavorable relation between the radius of the metal and the space available for it within the isoindole group.¹³

(12) F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

(13) P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1719 (1936).

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The Effect of Ionic Hydration on Rate and Equilibrium in Concentrated Alkaline Solutions. I. The H_- Function in Aqueous Alkaline Solutions and the Hydration of the OH^- Ion¹

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The values of the indicator acidity function H_- in concentrated aqueous NaOH and KOH solutions were calculated by applying the theory of Bascombe and Bell to alkaline solutions. It was found that the assumption of a hydration number of three for the OH^- ion, as suggested by Ackermann, leads to calculated values which are in good agreement with the experimental results of Schwarzenbach and Sulzberger.

The indicator acidity function^{2b} concept has been extensively applied in the interpretation of rate data of acid-catalyzed reactions in concentrated acid solutions.^{2a,b} Little work has been carried out concerning base-catalyzed reactions in concentrated alkaline solutions. The H_- function has been measured in methanolic alkaline solutions^{3a} and it was shown that the rate of a typical B-1 reaction, namely the hydrolysis of chloroform, follows that function in concentrated methoxide solutions.^{3b} The values of H_- in aqueous solutions of NaOH and KOH had been determined by Schwarzenbach and Sulzberger.⁴ These values were criticized on account of the method of measurement.⁵ However, recently reported rate data show nearly linear correlation with the experimental values of Schwarzenbach for H_- ; the reactions measured include the hydrolysis of chloramine and dimethylchloramine⁶ and the reaction of chloramine with ammonia.⁷ It is

(1) Presented before the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

(2) (a) L. Zucker and L. P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1939); (b) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

(3) (a) J. H. Ridd, *Chem. Ind. (London)*, 1268 (1957); (b) M. F. L. Allison, C. Bumford, and J. H. Ridd, *ibid.*, 718 (1958).

(4) G. Schwarzenbach and R. Sulzberger, *Helv. Chim. Acta*, **27**, 348 (1948).

(5) J. M. Flournoy and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 2257 (1961).

(6) M. Anbar and G. Yagil, *ibid.*, **84**, 1790 (1962).

the purpose of this and the following publication⁸ to evaluate the information which can be obtained on the mechanism of a base-catalyzed reaction from rate measurements in concentrated alkaline solutions. In this first part, a current theory regarding the origin of the acidity function phenomenon will be applied to alkaline solution, leading to a discussion of the state of hydration of the hydroxyl ion in these solutions. This information will be applied in part II⁸ to formulate the relations between reaction rate and basicity, and some experimental data supporting the conclusions will be presented.

The indicator acidity functions, treated originally as empirical concepts, have recently been rationalized by Bascombe and Bell,^{9,10} who showed that the high acidities encountered in concentrated acid solutions are primarily due to the strong hydration of the proton in these solutions. The existence of protons in a tetrahydrated form (H_3O_4^+) has been suggested by many investigators using a variety of experimental techniques.¹¹⁻¹⁷ When the hydration of the proton is

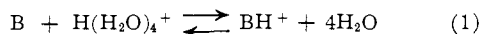
(7) G. Yagil and M. Anbar, *ibid.*, **84**, 1797 (1962).

(8) M. Anbar, M. Bobtelsky, D. Samuel, B. Silver, and G. Yagil, *ibid.*, **85**, 2380 (1963).

(9) K. N. Bascombe and R. P. Bell, *Discussions Faraday Soc.*, **24**, 158 (1957).

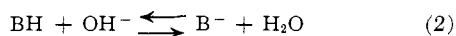
(10) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 81 ff.

taken into account, acid-base equilibria with acid-base indicators may be written



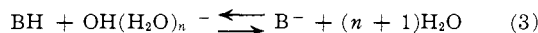
where B and BH⁺ are the two conjugate forms of the acid-base pair. The H₂O term on the right side of this equilibrium represents water not bound to the proton, hence to be called *free water*. It is evident that the free water concentration affects the equilibrium to the fourth power. The concentration of free water in concentrated acid solutions diminishes appreciably with increasing acid concentration; consequently there is a large increase in the BH⁺/B ratio, which determines the *H*₀ function. Insertion of numerical values, for acid and free water concentrations, into the equilibrium expression corresponding to eq. 3 will yield values of indicator ratios and of the indicator acidity function. Using this method of calculation, Bascombe and Bell obtained values of *H*₀ in the common acids which agreed with the observed values up to acid concentrations as high as 8 molar. The high indicator acidities observed in these solutions could thus be both qualitatively and quantitatively explained. Several assumptions inherent in these calculations will be discussed below.

The values of the *H*₋ function in alkaline solution, which represents the equilibrium



increase sharply with concentration.^{4,5} This suggests that the theory of Bascombe and Bell might be applicable to alkaline solutions as well. The object of part I is to examine this proposition and to derive a hydration number of the hydroxyl ion.

When hydration is taken into account, acid-base equilibria involving the hydroxide ion might be expressed by



where *n* is the hydration number of OH⁻. The equilibrium constant for this equation will be

$$K = a_B a_{H_2O}^{n+1} / a_{BH} a_{OH^-} \quad (4)$$

Following the arguments of Bascombe and Bell⁹ it will be assumed that the ratio of the activity coefficients is equal to unity; the validity of this will be discussed below. A molar equilibrium constant can, therefore, be applied.

$$K_c = C_B C_{H_2O}^{n+1} / C_{BH} C_{OH^-} \quad (5)$$

where *C*_{BH} is the stoichiometric molar concentration of OH⁻, and *C*_{H₂O} denotes the molar concentration of *free water* only.¹³

The *H*₋ indicator acidity function is defined¹⁹

$$H_- = \log \frac{C_{B^-}}{C_{BH}} \frac{1}{K_{BH}} \quad (6)$$

where *K*_{BH} denotes the conventional acid dissociation constant of BH. Inserting the value of *K*_c into this

(11) E. Wicke, M. Eigen, and T. Ackermann, *Z. physik. Chem.* (Frankfurt), **1**, 340 (1954).

(12) E. Glueckauf and J. P. Kitt, *Proc. Roy. Soc.* (London), **A228**, 322 (1955).

(13) E. Glueckauf, *Trans. Faraday Soc.*, **51**, 1235 (1955).

(14) M. Eigen and L. De Maeyer, "The Structure of Electrolyte Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p. 64.

(15) T. Ackermann, *Discussions Faraday Soc.*, **24**, 180 (1957).

(16) H. D. Beckey, *Z. Naturforschung*, **15a**, 822 (1960).

(17) D. G. Tuck and R. M. Diamond, *J. Phys. Chem.*, **65**, 193 (1961).

(18) All water concentrations in this and the subsequent paper will be normalized by dividing by 55.5, since equilibrium constants and observed rate constants are usually computed on the assumption that in dilute solution the concentration of water is unity, instead of 55.5.

(19) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

expression one obtains

$$H_- = \log \frac{C_{OH^-}}{C_{H_2O}^{n+1}} + \log \frac{K_c}{K_{BH}} \quad (7)$$

As shown below, the second term is simply p*K*_w. If one assumes a certain value for *n*, one can compute *C*_{H₂O} for different values of *C*_{OH⁻} (eq. 9 below). By inserting these values in the formula above, *H*₋ may be computed.

Before presenting the results of these calculations, the concentration scale to be used must be determined. Bascombe and Bell applied the molar concentration scale. Objections may be raised against the application of this scale in highly concentrated solutions and the same applies to the use of the molal scale. Alternatively, a mole-fraction scale may be used, but it remains unclear whether the cation and anion should be counted separately when the total number of moles is summed up.

Another scale which could be used is the volume fraction scale. It was shown by Glueckauf^{13,20} that the use of this scale facilitates the calculation of activity coefficients of electrolytes in concentrated solutions. The model of electrolyte solutions used in those calculations is that of Stokes and Robinson^{21,22} and is essentially the same model which is implied in the present calculation, namely that the rise in activity is connected with the decrease in free water concentration. The volume fraction scale takes care of departures from ideality which arise from differences in size between the various species in the system. It is evident that the differences in size between, say, a free water molecule and a tetrahydrated ion are not negligible, so that the use of the volume fraction scale may be justified (*cf.*, however, ref. 22, p. 244). Recognizing the uncertainty the use of each of these concentration scales, *H*₋ has been calculated using separately the molar, the mole fraction, and the volume fraction scales.

Calculation by the Molar Scale.—*K*_{BH} is determined² by the extrapolation of the measured values to infinite dilution, where the (normalized) concentration of water approaches unity. Keeping this in mind, one readily sees that log (*K*_c/*K*_{BH}) = p*K*_w. The value of p*K*_w at 20° is 14.166.²³ Inserting p*K*_w into 7, one obtains the final form of *H*₋ at 20°

$$H_- = 14.166 + \log C_{OH^-} - (n+1) \log C_{H_2O} \quad (8)$$

*C*_{H₂O}, the free water concentration, is calculated from

$$C_{H_2O} = d - 0.001(M + 18.0n) C_{OH^-} \quad (9)$$

where *d* is the density of the solution and *M* the formal weight of the alkali hydroxide (40.0 for NaOH and 56.1 for KOH). The values of *d* were taken from Åkerlöf and Kegeles²⁴ for NaOH and from Åkerlöf and Bender²⁵ for KOH.

Calculation by the Mole Fraction Scale.—The acid-base equilibrium may be expressed using mole fractions

$$K_x = \frac{X_{B^-}}{X_{BH}} \frac{X_{H_2O}^{n+1}}{X_{OH^-}} \quad (10)$$

Remembering that the indicator is present in the measured system at low concentrations, it may be assumed that *X*_{B⁻}/*X*_{BH} is equal to *C*_{B⁻}/*C*_{BH}; thus

$$H_- = \log \frac{C_{B^-}}{C_{BH}} \frac{1}{K_{BH}} = \log \frac{X_{B^-}}{X_{BH}} \frac{1}{K_{BH}} = \log \frac{X_{OH^-}}{X_{H_2O}^{n+1}} \frac{K_x}{K_{BH}} \quad (11)$$

In dilute solutions at 20°, *C*_{OH⁻}/*X*_{OH⁻} = 55.5; therefore *K*_x/*K*_{BH} = 55.5/*K*_w and

$$H_- = 14.166 + \log 55.5 X_{OH^-} - (n+1) \log X_{H_2O} \quad (12)$$

(20) E. Glueckauf, in ref. 14, p. 97.

(21) (a) R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.*, **70**, 1870 (1948); (b) R. H. Stokes and R. A. Robinson, *Trans. Faraday Soc.*, **53**, 301 (1953).

(22) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth, London, 1959, p. 248 ff.

(23) H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1949).

(24) G. Åkerlöf and G. Kegeles, *J. Am. Chem. Soc.*, **61**, 1027 (1939).

(25) G. Åkerlöf and P. Bender, *ibid.*, **63**, 1085 (1941).

which is the formula used for calculation; X_{OH^-} (hydrated) and $X_{\text{H}_2\text{O}}$ (of free water) were computed from

$$X_{\text{OH}^-} = \frac{C_{\text{OH}^-}}{2C_{\text{OH}^-} + C_{\text{H}_2\text{O}}} \quad X_{\text{H}_2\text{O}} = \frac{C_{\text{H}_2\text{O}}}{2C_{\text{OH}^-} + C_{\text{H}_2\text{O}}}$$

where $C_{\text{H}_2\text{O}}$ was calculated as described above, using nonnormalized values. The cation and anion were counted as two separate species.

Calculation by the Volume Fraction Scale.—The volume fraction V_i of a component in a solution is given by

$$V_i = \frac{n_i \bar{V}_i}{V} = C_i \bar{V}_i \quad (13)$$

where n_i denotes the number of moles of the component i in the total volume V , and \bar{V}_i denotes the partial molal volume of the component.

The acid-base equilibrium expression to be applied in the volume fraction calculation is

$$K_v = \frac{V_{\text{B}^-} V_{\text{H}_2\text{O}}^{n+1}}{V_{\text{BH}} V_{\text{OH}^-}} \quad (14)$$

Indicator molecules used in H_- determinations are fairly large organic molecules and the relation $V_{\text{B}^-}/V_{\text{BH}} = C_{\text{B}^-}/C_{\text{BH}}$ will hold. Combining this with K_v and introducing into the definition of H_- one obtains

$$H_- = \log \frac{C_{\text{B}^-}}{C_{\text{BH}} K_{\text{BH}}} = \log \frac{V_{\text{OH}^-}}{V_{\text{H}_2\text{O}}^{n+1}} + \log \frac{K_v}{K_{\text{BH}}} \quad (15)$$

The second term in this case is equal to $\log 1/\bar{V}_{\text{OH}^-}^{\circ} K_w$, where $\bar{V}_{\text{OH}^-}^{\circ}$ denotes the partial molal volume of the (hydrated) hydroxide at infinite dilution. The values of H_- at 20° may then be calculated by

$$H_- = 14.166 + \log \frac{V_{\text{OH}^-}}{\bar{V}_{\text{OH}^-}^{\circ}} - (n+1) \log V_{\text{H}_2\text{O}} \quad (16)$$

The volume fractions of the hydrated hydroxide were derived from partial molar volumes by eq. 13. The partial molal volumes were derived from apparent molal volumes by the relation $\bar{V}_2 = n_2 \partial\phi/\partial n_2 + \phi$ (subscript 2 denoting solute).²⁶ From the definition of the apparent molal volume, $\phi = (V - n_1 \bar{V}_1^0)/n_2$, it is evident that the apparent molal volume of the hydrated solute exceeds that of the nonhydrated solute by $n \bar{V}_1^0 = 18n$ ml./mole.^{21b} This term was consequently added to the values of the nonhydrated hydroxide to yield ϕ of the hydrated hydroxide; ϕ values of unhydrated species were taken from Åkerlof, *et al.*^{24,25} To obtain \bar{V}_2 values of $\partial\phi/\partial n_2$ are also needed and these were taken from the empirical relations between ϕ and m given by Åkerlof. Upon addition of $18n$ ml./mole to the partial molal volumes of hydroxides at infinite dilution, these no longer show negative values, a fact which encourages the hydration approach.

The volume fraction of free water was calculated by

$$V_{\text{H}_2\text{O}} = 1 - V_{\text{OH}^-} \quad (17)$$

The result of computations based on hydration number $n = 3$ are given in Tables I and II. Columns 4, 5, and 6 show the calculated values of H_- in KOH and NaOH on the molar scale, the mole fraction scale, and the volume fraction scale, respectively. It can be seen that the differences between the three scales are not large. The observed values of Schwarzenbach and Sulzberger,⁴ corrected as explained in Table I, are shown in column 7. On the molar scale, the calculated values in NaOH agree with the observed ones up to 7 M hydroxide, while in KOH they are somewhat low. On the volume fraction scale the agreement is very good in KOH, while in NaOH the calculated values are somewhat high (a fractional hydration number 2.8 giving the best fit). On the mole fraction scale the calculated values are somewhat lower in both KOH and NaOH. Calculations based on either $n = 2$ or $n = 4$ lead to values considerably different from the experimental ones in both solutions on any of the three scales. It is evident that the theory of Bascombe and Bell^{9,10} is applicable to concentrated alkaline solutions and leads to the conclusion that three moles of water are associated with each mole of hydroxide ion, which may be formulated as $\text{OH}(\text{H}_2\text{O})_3^-$.

(26) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 358 ff.

TABLE I
CALCULATED AND OBSERVED VALUES OF H_- IN AQUEOUS SOLUTIONS OF KOH

$T = 20^\circ, n = 3$

C_{KOH}, M	$C_{\text{H}_2\text{O}}^{a,b}$	$V_{\text{H}_2\text{O}}^a$	H_- calculated			H_- obsd. +0.27 ^c
			Molar scale	M. F. sc.	V. F. sc.	
1	0.942	0.937	14.27	14.24	14.31	(14.27)
2	.875	.869	14.70	14.63	14.77	14.79
3	.807	.800	15.02	14.90	15.10	15.10
4	.738	.730	15.30	15.14	15.39	15.40
5	.665	.654	15.57	15.35	15.68	15.74
6	.592	.585	15.85	15.57	15.96	16.07
7	.522	.512	16.14	15.80	16.25	16.40
8	.450	.440	16.47	16.07	16.58	16.77
10	.298	.293	17.25	16.73	17.40	17.55

^a Subscript H_2O denotes free water. ^b Normalized molarity.¹⁸

The observed values are taken from Schwarzenbach and Sulzberger.⁴ These authors assumed an arbitrary value of $H_- = 14.00$ at $\text{KOH} = 1 M$. In order to facilitate comparison, we assumed that H_- for 1 M KOH is 14.27, the calculated value on the molar scale. Consequently, 0.27 has been added to all observed values (part of the difference is due to the pK_w value of 14.166 used by us instead of 14.00 as used by Schwarzenbach). Comparison with the mole fraction scale values requires the subtraction of 0.03 from the last column, whereas comparison with volume fraction scale values requires the addition of 0.04 to the same column.

TABLE II
CALCULATED AND OBSERVED VALUES OF H_- IN AQUEOUS SOLUTIONS OF NaOH, $T = 20^\circ, n = 3$

C_{OH^-}, M	$C_{\text{H}_2\text{O}}^b$	$V_{\text{H}_2\text{O}}$	H_- calculated			H_- obsd. +0.26
			Molar scale	M. F. sc.	V. F. sc.	
1	0.945	0.947	14.26	14.24	14.31	(14.26) ^a
2	.890	.889	14.66	14.62	14.73	14.62
3	.832	.829	14.95	14.88	15.05	14.95
4	.778	.767	15.20	15.10	15.31	15.18
5	.715	.704	15.44	15.31	15.57	15.44
6	.650	.640	15.69	15.52	15.82	15.64
7	.588	.575	15.93	15.70	16.08	15.85
8	.525	.509	16.19	15.91	16.35	16.10
10	.390	.378	16.80	16.43	16.97	16.50

^a See explanation to Table I. In Table II, 0.26, the calculated value at $C_{\text{OH}^-} = 1 M$ on the molar scale minus 14.00, was added to the observed values of Schwarzenbach and Sulzberger.⁴ Further corrections of -0.02 and $+0.05$ should be made in the last column when the calculated values on the mole fraction and volume fraction scales are compared with the observed data.

^b Normalized molarity.¹⁸

It should be mentioned at this point that the observed H_- values were obtained in systems which contain an immiscible solvent in addition to the hydroxide solution.⁴ Certain assumptions regarding the ratios of activity coefficients and distribution coefficients have to be made in order to make the measured values applicable to the aqueous hydroxide solution. Yet the fact that the rate dependence on the observed H_- values of several reactions is almost linear^{6,7} indicates that the above-mentioned ratios are not far from unity; recent measurements on the dissociation of thioacetamide in NaOH²⁷ also confirm Schwarzenbach and Sulzberger's values. Nevertheless, the conclusions reached here should not be regarded as final until better experimental values of H_- are available.

Additional assumptions and simplifications inherent in our calculations, as well as in those of Bascombe and Bell, will now be discussed.

First, in using the pseudo-equilibrium constants K_c , K_w , K_v , it has been assumed that the activity coefficient ratios are equal to unity; this may be justified in view of the theories of Stokes and Robinson^{21,22} and of Glueckauf^{13,20} concerning the thermodynamic

(27) J. T. Edward and I. C. Wang, *Can. J. Chem.*, **40**, 399 (1962).

behavior of concentrated electrolytic solutions. Stokes and Robinson show that when hydration is taken into account, most of the deviation from ideality disappears, and the remaining deviations can be accounted for by the electrostatic interaction, as given by the expression $\log f = A\mu^{1/2}/(1 + B\delta\mu^{1/2})$. The ion size parameter δ of KOH (3.70 Å.) and NaOH (3.25 Å.)²⁸ is not very different from most other salts; consequently the electrostatic contribution to the activity coefficient ratio will be negligible. In Glueckauf's treatment deviations from ideality due to differences in the size of the species involved are taken into account by using the volume fraction scale; this treatment results in a more consistent set of hydration numbers for cations and anions. As the volume fraction scale was applied in the present calculations, the overlooking of activity coefficients is in line with current ideas regarding the behavior of concentrated electrolyte solutions.

It has been recently proposed by Edward and Wang,²⁷ who made a similar calculation to the present one, that the effect of activity coefficients may be included in the exponent n . This cannot be entirely ruled out, yet it should be noted that when dealing with equilibrium activity coefficients of hydrated species in free water should be considered and not conventional activity coefficients, as has been done in their derivations (the connection between the two kinds of activity coefficients has been discussed by Robinson and Stokes^{21,22} and by Glueckauf).²⁰ Consequently, the contribution of activity coefficients to n should be much smaller than implied by Edward and Wang.

Second, it was assumed that the indicator in the form of B⁻ is nonhydrated or rather not more hydrated than BH.²⁹ Glueckauf¹³ finds that any anion larger than Cl⁻ may be considered as nonhydrated in the thermodynamic sense. As the indicator molecules are generally relatively large organic molecules, the assumption seems justified.

Third, the departure of the calculated values from the experimental ones in solutions in which hydroxide concentration exceeds 7 M is expected since these solutions contain less than 50% free water by volume (column 3 in Tables I and II). Above 14 M hydroxide solution, there is no water to form a trihydrated species; therefore, these solutions must consist of dihydrated, monohydrated, or even nonhydrated species.

Last, the water of hydration of the cation, if any, was counted as free water. The fact that almost the same degree of hydration was found for both hydroxides indicates that this approximation was justified. However, Glueckauf¹³ finds numbers of hydration $n = 0.6$ for K⁺ and $n = 2.0$ for Na⁺. An explanation which will not invalidate the picture presented in this study and still be consistent with the presence of water of hydration of the cation is the possibility that one or more molecules of water are simultaneously attached to both OH⁻ and Na⁺. This means that NaOH in concentrated solution exists mainly in the form of water-bridged ion-pairs, the oxygen of the water being attached to the cation and the hydrogen to the hydroxide ion. Such water-bridged ion-pairs were suggested 20 years ago by Robinson and Harned³¹ to explain the

thermodynamic behavior of concentrated hydroxide solutions. The chemical shift observed in the proton magnetic resonance of concentrated NaOH³² supports this idea. Such a configuration of hydrated NaOH may account for the diminished conductivity as well as other deviations from expected behavior which have led several authors to attribute a measurable dissociation constant to NaOH in concentrated solutions.³³ The high values of H_- encountered in these solutions are certainly incompatible with the existence of an appreciable amount of NaOH in undissociated form; neither is the existence of an appreciable concentration of ion pairs of the usual type to be expected in concentrated NaOH solutions.

The present model can account only for small variations of H_- with temperature, due to variations of density of the solutions concerned. No data concerning the variation of H_- with temperature are available, yet the information regarding variation of H_0 with temperature suggest that these are not large.³⁴

Summing up, it seems that in spite of all the simplifications inherent in the calculations performed, the formula OH(H₂O)₃⁻ may in fact represent the state of the hydroxide ion in solution. This conclusion is in accord with other findings: the existence of this species has been suggested by Ackermann¹⁵ on the basis of heat capacity measurements and has also been postulated in the interpretation of the conductivity of ice.³⁵ The calculations based on activity coefficient data¹³ lead to similar conclusions, although a somewhat higher number of hydration, $n = 4$, has been arrived at. Measurements of Raman spectra,³⁶ infrared spectra,³⁷ and ionic entropy data³⁸ also indicate that in aqueous solutions OH⁻ exists in a strongly hydrated form, different in character from most other anions (with the exception of the small F⁻ ion).

As mentioned in the Introduction there is a large body of evidence for the hydrated H⁺ ion—[H₉O₄]⁺; OH(H₂O)₃⁻ ([H₇O₄]⁻) differs from the last species by two protons, and a similar structure of four oxygens may be involved. Two alternative structures can be proposed for such a species; either all three water molecules are bound to the oxygen of the OH⁻ ion (Fig. a) or one water molecule is bound to the hydrogen of the OH⁻ ion (Fig. b). However, OH⁻, being a very

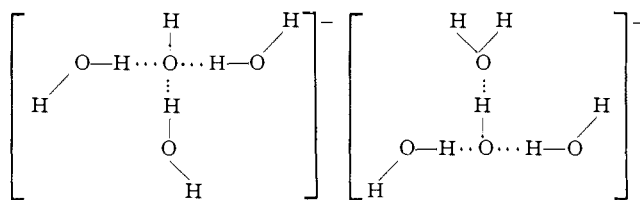


Figure a.

Figure b.

strong base, is much more likely to form a hydrogen bond by accepting an H than by donating it. The fact that the high frequency OH⁻ mode of the Raman spectrum remains unchanged when an alkali hydroxide is dissolved in water³⁶ corroborates this; the structure of the hydroxide ion shown by Fig. a is thus the more likely one. Three oxygen atoms are then available to form a water-bridged ion pair.

It may be concluded that a fair amount of evidence

(28) H. S. Harned and B. B. Owen, ref. 26, Table 12-5-2.

(29) In this connection it should be mentioned that it has been proposed by Taft³⁰ that the difference between H_R and H_0 in concentrated acid solutions can be explained if one assumes that indicators used to determine H_0 are hydrated by three water molecules in the base form while those used to determine H_R are not. This hypothesis contradicts, however, the theory of Bascombe and Bell. The behavior of the H_R acidity function may still be interpreted as involving an equilibrium between a nonhydrated B⁺ and hydrated BOH form (BOH contains three hydrogen bonding sites not present in B⁺).

(30) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960).

(31) R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 455 (1941).

(32) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

(33) Cf. F. G. R. Gimblett and C. B. Monk, *Trans. Faraday Soc.*, **50**, 965 (1954).

(34) Reference 2, p. 945.

(35) M. Eigen and L. de Mayer, *Proc. Roy. Soc. (London)*, **A247**, 505 (1958).

(36) W. R. Busing and D. F. Hornig, *J. Phys. Chem.*, **65**, 284 (1961).

(37) T. Ackermann, *Z. physik. Chem. (Frankfurt)*, **27**, 253 (1961).

(38) H. S. Frank in Abstracts of Papers presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, p. 1T.

has been presented for the existence of a trihydrated hydroxyl ion, whatever its lifetime and its exact configuration might be. Concentrated solutions of the hydroxides can thus be pictured as solutions of a hydrated hydroxide ion in free water. Although more refined theories regarding the structure of free water and aqueous solutions in general³⁹⁻⁴¹ may require some

modification in this model, it seems to account well enough for the properties discussed. An attempt to interpret rate data in these solutions by this model will therefore be presented in the following paper.⁸

(39) A. Eucken, *Z. Elektrochem.*, **52**, 255 (1948).

(40) W. Kangro, *Z. physik. Chem. (Frankfurt)*, **32**, 273 (1962).

(41) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962):

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The Effect of Ionic Hydration on Rate and Equilibrium in Concentrated Alkaline Solutions. II. The Kinetics of Base-Catalyzed Reactions in Concentrated Hydroxide Solutions^{1a}

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Equations are derived which relate the observed rate constants of various base-catalyzed reactions with the indicator basicity of the solution as expressed by the H_- function. Assuming that the hydroxide ion is a trihydrated species, the rate equations were expressed also in terms of C_{OH^-} , the stoichiometric concentration of hydroxide ion, and of C_{H_2O} , the concentration of "free" water. It is concluded that the rate dependence in concentrated alkaline solution primarily indicates the change in the number of water molecules involved in the formation of the transition state. In the cases of nucleophilic substitution by a nonhydrated hydroxide, as well as in a proton abstraction reaction, a rate law obeying C_{OH^-}/C_{H_2O} is derived. These equations have been verified experimentally in the cases of hydrolysis of ethyl iodide, a typical S_N2 reaction, and in the breakdown of serine phosphate in basic solution which has been shown to proceed by a mechanism involving proton abstraction.

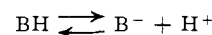
The kinetic behavior of acid-catalyzed reactions in concentrated acid solution has been the subject of increasing interest for some time. Considerable data have been accumulated,² the interpretation of which has been the subject of discussion ever since Zucker and Hammett advanced their original hypothesis.³ This hypothesis states that reactions whose rate follows the appropriate indicator acidity function operate through a unimolecular conversion of the active species, while reactions whose rate tends to follow the stoichiometric acidity of the solution operate by a bimolecular reaction of the active species with solvent water.

Little attention has been paid in the past to reactions in concentrated basic solutions. Only recently have rate measurements been conducted in concentrated aqueous KOH and NaOH^{4a,b} and in alkaline methanol.⁵ In each of these reactions a correlation of the rate with the H_- acidity function was found. It was therefore of interest to evaluate what information on the mechanism can be obtained from this relationship in more general cases.

A formal derivation based on an approach analogous to that employed in the interpretation of acid-catalyzed reactions can be presented for each type of base-catalyzed mechanism correlating the observed rate constant with the H_- acidity function. Taking into consideration that the hydroxide ion is strongly hydrated, most probably as a trihydrated ion, it was shown⁶ in analogy to the approach used by Bascombe and Bell⁷ that the H_- function may be expressed in terms of concentrations of hydroxide ions and of "free" water. Consequently, the rate equations of base-catalyzed reactions in con-

centrated alkaline solutions may also be expressed in terms of hydrated hydroxide ion concentration and of "free water." The use of this form of the equations can lead to a better understanding of the mechanism of base-catalyzed reactions. Also it does point out the limitations of the use of the equations, as will be considered in the discussion.

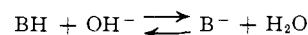
Mechanisms of Base-Catalyzed Reactions. Definitions.—The notation used here is that employed by Long and Paul^{2a} in their discussion of acid-catalyzed reactions; H_- is defined^{2b} by $H_- = -\log (C_{BH}/C_B^-)K_{BH}$ where K_{BH} is the acid dissociation constant of an indicator dissociating according to



h_- is defined^{2b} by the equation $H_- = -\log h_-$; hence

$$h_- = \frac{C_{BH}}{C_B^-} K_{BH} = \frac{f_{B^-} a_{H^+}}{f_{BH}} = \frac{f_{B^-} a_{H_2O}}{f_{BH} a_{OH^-}} K_w$$

In alkaline solutions the dissociation of BH can also be described by



Consequently one can define b_- as

$$b_- = K_w/h_- = f_{BH} a_{OH^-} / f_{B^-} a_{H_2O} \quad (1)$$

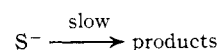
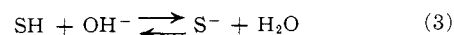
This quantity has the advantage that it is directly related to the OH^- activity and in dilute alkaline solutions, where the activity coefficients approach unity, it approaches C_{OH^-} . The function b_- is thus the alkaline counterpart of h_0 in acid solution. A consequence of eq. 1 is the relation

$$f_{BH}/f_{B^-} = b_-(a_{H_2O}/a_{OH^-}) \quad (2)$$

which will be used in the discussion which follows.

Each of the main types of reaction which can occur in alkaline solution will now be dealt with in more detail.

Case I.—The substrate SH is in rapid pre-equilibrium with its conjugated base S^- ; S^- is then converted to the products of the reaction in a unimolecular rate-determining step



(1) (a) Presented before the 140th National Meeting of the American Chemistry Society, Chicago, Ill., September, 1961; (b) The Research Laboratories of the Israel Atomic Commission, Rehovoth, Israel.

(2) (a) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957); (b) M. A. Paul and F. A. Long, *ibid.*, **57**, 1 (1957); (c) H. Zollinger, *Ann. Rev. Phys. Chem.*, **13**, 391 (1962).

(3) I. Zucker and L. P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1939).

(4) (a) M. Anbar and G. Yagil, *ibid.*, **84**, 1790 (1962); (b) G. Yagil and M. Anbar, *ibid.*, **84**, 1797 (1962).

(5) M. F. L. Allison, C. Bumford, and J. H. Ridd, *Chem. Ind. (London)*, 718 (1958).

(6) G. Yagil and M. Anbar, *J. Am. Chem. Soc.*, **85**, 2376 (1963), to be referred to as Part I.

(7) (a) K. N. Bascombe and R. P. Bell, *Discussions Faraday Soc.*, **24**, 158 (1957); (b) R. P. Bell, "The Proton in Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1959, p. 81 ff.