

The Equilibrium between Ethoxide and Hydroxide Ions in Ethanol and in Ethanol-Water Mixtures.

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The equilibrium constant for the reaction



in ethanol-water at 25° has been determined. In mixtures containing a few per cent. of water, and in pure ethanol, the equilibrium favours ethoxide ion. It is deduced that solutions made by dissolving alkali hydroxides in ethanol will contain mainly ethoxide ion rather than hydroxide. For instance, in a 0.1M-solution of sodium hydroxide in 99% ethanol, 96% of the total base is ethoxide. Solutions made by dissolving sodium in ethanol or aqueous ethanol are also considered. The relative acid dissociation constants of ethanol and water, in (a) ethanol, and (b) water, are estimated; in each solvent they differ by less than a power of 10.

SEVERAL pieces of experimental evidence suggest that in pure ethanol, and in ethanol-water mixtures containing not more than a few per cent. of water by weight, the equilibrium



lies in favour of the ethoxide ion. For example, the rate of the hydrolysis of an ester in ethanol-water to which hydroxide has been added becomes vanishingly small as the amount of water in the solvent approaches zero (Wegscheider and Ripper, *Sitzungsber. Akad. Wiss., Vienna*, 1918, 127, IIb, 129). This suggests that the concentration of hydroxide ion, which is the only ion present capable of hydrolysing the ester, approaches zero in solutions of low water content. Again, by infra-red spectroscopy, Williams and Bost (*J. Chem. Phys.*, 1936, 4, 251) measured the amount of water produced when sodium hydroxide was dissolved in dry ethanol, and found that it corresponded to conversion of 75—100% of the hydroxide ion into ethoxide ion.

The thermodynamic equilibrium constant for reaction (1) in ethanol-water is given for any solvent composition by :

$$K = \frac{[\text{OH}^-]a_a}{[\text{OEt}^-]a_w} \cdot \frac{\gamma_{\text{OH}^-}}{\gamma_{\text{OEt}^-}} \quad (2)$$

where the square brackets indicate molar concentrations; a_w and a_a are the activities of water and ethanol with respect to the pure liquids, and are known; and γ_{OEt^-} and γ_{OH^-} are the activity coefficients of ethoxide and hydroxide ions in any solvent mixture, the standard state being taken as the infinitely dilute solution in that solvent mixture. Since, however,

there are no data on $\gamma_{\text{OH}^-}/\gamma_{\text{OEt}^-}$, we must make use of the quantity K' defined by the equation:

$$K' = \frac{[\text{OH}^-]a_a}{[\text{OEt}^-]a_w} = K \frac{\gamma_{\text{OEt}^-}}{\gamma_{\text{OH}^-}} \quad \dots \quad (3)$$

K' is not a true thermodynamic constant, and its value will not be independent of the solvent composition, except at very low base concentrations.

It is convenient to define a third quantity, K° , by the following equation, in which $[\text{H}_2\text{O}]$ stands for the molar concentration of water:

$$K^\circ = [\text{OH}^-]/[\text{OEt}^-][\text{H}_2\text{O}] = K'a_w/a_a[\text{H}_2\text{O}] \quad \dots \quad (4)$$

This quantity is of interest in solutions of low water content. In such solutions, a_a is nearly unity, while the ratio $a_w/[\text{H}_2\text{O}]$ may be found from the Henry's law constant for dilute solutions of water in ethanol (from vapour pressure data in Landolt-Börnstein's "Tabellen," Springer, Berlin, 5th ed., 1931, Erg. IIb, p. 1130), which gives $a_w = 0.16 [\text{H}_2\text{O}]$. Thus we find from (4) that K° in l. mole⁻¹ is given in ethanol by:

$$K^\circ = 0.16 \text{ (limiting value of } K' \text{ at low water concentration)} \quad \dots \quad (5)$$

It is possible to obtain an estimate of the magnitude of K° , and hence of K' , in ethanol, from the data of Hine and Hine (*J. Amer. Chem. Soc.*, 1952, **74**, 5266) who measured the equilibrium constants for the reactions of isopropoxide ion with both hydroxide and ethoxide ions in isopropanol. The ratio of these constants gives the equilibrium constant for the reaction (1). The value obtained is $[\text{OH}^-][\text{EtOH}]/[\text{OEt}^-][\text{H}_2\text{O}] = 1.27$. If we suppose that a change of solvent from isopropanol to ethanol does not alter the ratio of the activity coefficients of the ions, and if we put the concentration of EtOH in ethanol as 17 moles/l., this gives $K^\circ = 0.074$ l./mole, and hence $K' = 0.46$ in ethanol.

These results imply that when caustic alkali is added to ethanol the resulting solution contains much more ethoxide ion than hydroxide. This conclusion is of such general interest that an independent determination of K' is desirable. In the present investigation (of which a preliminary report was given in *Nature*, 1953, **172**, 583), the equilibrium constant K' has been measured at 25° in five ethanol-water mixtures containing from 12.6 to 47.0% of water by weight, by a colorimetric method; 2:4:6-trinitrotoluene was used as indicator, ionising in ethanol in the presence of a strong base to give a purple solution (Caldin and Long, to be published).

The equation used in the colorimetric determination of K' can be derived as follows. The coloured ion of trinitrotoluene is presumed to be produced by reaction with ethoxide or with hydroxide ion, and destroyed by reaction with ethanol or water. The reactions are (writing trinitrotoluene as BH)



Since we have no data on γ_{BH} , $\gamma_{\text{B}^-}/\gamma_{\text{OEt}^-}$, or $\gamma_{\text{B}^-}/\gamma_{\text{OH}^-}$, we must use, in place of K_a and K_w , quantities K'_a and K'_w , defined as follows and not necessarily independent of composition:

$$K'_a = [\text{B}^-]a_a/[\text{OEt}^-][\text{BH}] \quad \dots \quad (8)$$

and

$$K'_w = [\text{B}^-]a_w/[\text{OH}^-][\text{BH}] \quad \dots \quad (9)$$

so that

$$K' = K'_a/K'_w \quad \dots \quad (10)$$

The total base concentration b , as found by titration with standard acid, is $b = [\text{OH}^-] + [\text{OEt}^-]$; the term $[\text{B}^-]$ is negligibly small. With equations (8) and (10), this relation gives:

$$[\text{HB}]/[\text{B}^-] = (a_a + a_w K')/b K'_a \quad \dots \quad (11)$$

Consideration of the rates of formation and destruction of the ion B^- gives the same equation.

The ratio $[HB]/[B^-]$ is related to the optical density, D , of the solution at a given wavelength. If ϵ is the molar extinction coefficient of the ion B^- , l the length of the light-absorption path, and d the initial concentration of HB, then $[B^-] = D/\epsilon l$ and $[HB] = d - D/\epsilon l$. Substituting in equation (11), we find :

$$d/D = 1/\epsilon l + (1/b)(a_a + a_w K')/\epsilon l K_a' \quad . \quad . \quad . \quad (12)$$

Hence a plot of d/D against $1/b$ will be linear, with an intercept which gives us the extinction coefficient ϵ of the coloured ion; and the ratio, R , of the intercept to the slope will be :

$$R = K_a'/(a_a + a_w K'), \text{ whence } K' = (K_a'/R - a_a)/a_w \quad . \quad . \quad (13)$$

From this expression K' has been determined as follows. Values of a_a and a_w were taken from vapour-pressure data as before. The value of R for each solvent mixture was obtained experimentally by measuring the optical density produced when a series of known volumes of base solution were added to a solution of trinitrotoluene contained in the reaction cell, about 8 measurements being made in each series. The base solutions were prepared by dissolving either sodium (for series 1 and 2) or sodium hydroxide (for series 3, 4, and 5) in the appropriate solvent mixture. The plot of d/D against $1/b$ was invariably linear within experimental error, and from the slope and intercept the ratio R could be determined within $\pm 5\%$. The value of K_a' is, as may be seen from equation (13), simply the value of R in pure ethanol, in which $a_w = 0$ and $a_a = 1$. If we assume as a first approximation that K_a' is a true constant, independent of solvent composition, we can use this value for all solvent mixtures. This approximation is considered below in the light of the results; it is the only approximation used in calculating K' from the observations. The experimental methods are described more fully in another paper (Caldin and Long, to be published) where also the value of K_a' , obtained as described above, is reported as 2040 ± 70 l. mole $^{-1}$ at 25° . It should perhaps be said that the evidence given in that paper does not exclude the possibility that the coloured species is a complex of trinitrotoluene with ethoxide ion, rather than an anion; if this were so, however, the mathematical treatment would be very similar, the numerical results would be of the same order, and our general conclusions would be unchanged.

TABLE 1. Results at 25.0° .

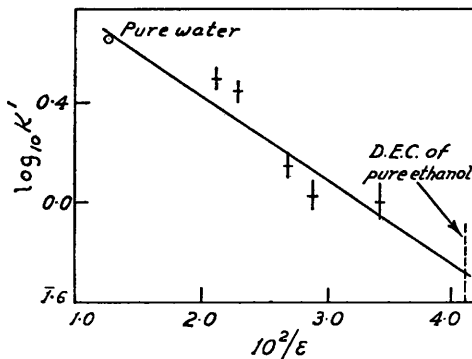
b = base concn. in mole l. $^{-1}$.
 d = trinitrotoluene concn. (mean) in mole l. $^{-1}$.
 ϵ = extinction coefficient in mole $^{-1}$ l. cm. $^{-1}$.
 R in l. mole $^{-1}$.

Series no.	Wt. % of water	a_a	a_w	$10^5 d$	Range of $10^3 b$	R	K'	$10^{-4} \epsilon$
1	12.6	0.762	0.516	1.1	0.19—2.84	1580	1.0 ± 0.2	1.30 ± 0.05
2	24.2	0.652	0.696	1.2	0.52—7.12	1470	1.1 ± 0.15	1.21 ± 0.05
3	28.8	0.623	0.734	1.1	0.39—6.68	1245	1.4 ± 0.2	1.22 ± 0.05
4	38.8	0.565	0.775	1.2	0.36—4.90	750	2.7 ± 0.3	1.27 ± 0.05
5	47.0	0.527	0.816	1.2	1.80—38.4	660	3.1 ± 0.3	1.24 ± 0.05

Table 1 summarises the experimental results, and the derived values of K' , calculated by equation (13), and of the extinction coefficient ϵ for the wave-length region used (about 0.5μ). It will be seen that the extinction coefficient does not change appreciably with solvent composition; this confirms the assumption that the concentration measured optically is that of the same species throughout. The values for K' vary less than the ratio of water to ethanol in the solvent; they do however vary systematically with the solvent composition. This variation could be due either to variations in the ratio $\gamma_{OEt^-}/\gamma_{OH^-}$, which relates K' to the true thermodynamic constant K [equation (3)]; or to variations in $\gamma_{B^-}/\gamma_{OEt^-} \cdot \gamma_{HB}$, which relates K_a' (used in deriving K') to the true thermodynamic constant K_a [equations (6) and (8)]; or to both. That the former is the more important factor is indicated by the following evidence. The effect of added ethanol on

the rate, in water, of the hydrolysis of esters by hydroxides was studied by Scaife (Thesis, Leeds, 1938). His results agree with the assumption that only hydroxide ion can bring about the reaction, and the reduction in rate on adding ethanol is quantitatively accounted for if $K' = 4.5$ in pure water. (It is unfortunately difficult to assess the accuracy of this estimate.) This value, which is independent of all values of K_a' , is in agreement with the trend of the values of K' given in Table 1, as may be seen from the Figure in which $\log_{10} K'$ is plotted against the reciprocal of the dielectric constant (ϵ) of the solvent. This agreement supports the view that variations in $\gamma_{\text{OEt}^-}/\gamma_{\text{HO}^-}$ are the main source of the variations in K' , rather than variations in K_a' . Thus our assumption that K_a' is to a first approximation independent of solvent composition seems to be justified.

A value of K' in pure ethanol may be obtained by extrapolation, from a plot of $\log_{10} K'$ against solvent composition, or against the reciprocal of the dielectric constant of the solvent mixture (Figure). We obtain, at 25° , $K' = 0.5 \pm 0.1$; whence $K^\circ = 0.08 \pm 0.02$ l. mole $^{-1}$. These values for the equilibrium constants in pure ethanol agree well with Hine and Hine's results in isopropanol. They are incidentally of the same order



Plot of $\log_{10} K'$ against reciprocal of dielectric constant (ϵ) of solvent mixture.

of magnitude as those for the corresponding equilibrium in methanol, for which Unmack found $K' \approx 1$ (*Z. physikal. Chem.*, 1928, 133, 45, and earlier papers).

The Composition of "Alcoholic Hydroxide" Solutions.—When sodium hydroxide is dissolved in ethanol or an ethanol-water mixture, the resulting solution will contain hydroxide and ethoxide ions in equilibrium. The relative concentrations of the two ions can be calculated from the preceding results. Let the initial molar concentration of water be c ; then the equilibrium concentration will, in virtue of equation (1), be $[\text{H}_2\text{O}] = c + [\text{OEt}^-]$. The total base concentration is $b = [\text{OH}^-] + [\text{OEt}^-]$. Combining these two equations with equation (4), we find $K^\circ = [\text{OH}^-]/(b - [\text{OH}^-])(c + b - [\text{OH}^-])$, whence by solving a quadratic we can find the fraction of base present as hydroxide, $[\text{OH}^-]/b$, in terms of b , c , and K° . The results for ethanol containing initially 0, 0.2, and 1.0% water by weight are given in Table 2. (Ethanol carefully treated to remove water

TABLE 2. Percentage of total base present as hydroxide in solutions made by dissolving sodium hydroxide in ethanol and some ethanol-water mixtures, at 25° .

Wt. % of water in solvent	Total base (%) present as hydroxide at		
	$b = 0.1M$	$0.5M$	$1.0M$
0	0.8	3.7	6.9
0.2	1.5	4.2	7.5
1.0	4.1	6.8	9.6

may contain 0.2% of water after a little handling in ordinary air.) We have used the value of $K^\circ = 0.08$ l. mole $^{-1}$ for pure ethanol, and have therefore confined our calculations to the range of base concentrations for which the final water concentration is not more than about 2% by weight. The effect of varying ionic strength on the ratio a_s/a_w has been neglected. It is clear from these figures that in such solutions most of the hydroxide added is converted into ethoxide. A similar conclusion will be true of methanol solutions. The

results refer to 25°, but are unlikely to be very different at temperatures up to the boiling point of ethanol.

The conclusion that when hydroxides are dissolved in ethanol (or methanol) the solution contains mainly ethoxide (or methoxide) rather than hydroxide ion throws light on several otherwise puzzling facts. (i) The addition of 1% of water has little effect on the rate or equilibrium of the reaction between ethoxide ion and trinitrotoluene or trinitrotriphenylmethane in ethanol (Caldin and Trickett, *Trans. Faraday Soc.*, 1953, **49**, 772; Caldin and Long, unpublished work). (ii) Baker and Neale (*Nature*, 1953, **172**, 583) observed nearly equal velocity constants for hydroxide and ethoxide in substitution and elimination reactions of benzyl nitrate in ethanol. (iii) In aromatic nucleophilic substitution reactions, use of "alcoholic hydroxide" solutions usually results in the introduction of an alkoxy- rather than a hydroxy-group. The rates of two such reactions—those of *o*-dinitrobenzene and of 1-chloro-2:4-dinitrobenzene—have been measured using hydroxide and ethoxide solutions, and in each case the two rates were very similar (Bunnett and Zahler, *Chem. Reviews*, 1951, **49**, 339, 340, 348). (iv) The conductances of solutions of sodium hydroxide and methoxide in methanol have similar values over a range of concentration, as have those of sodium hydroxide and ethoxide in ethanol; and the limiting conductances of the sodium hydroxide solutions are not abnormally large (Landolt-Börnstein, "Tabellen," Springer, Berlin, 5th edn., 1923, p. 1110; 1931, Erg. IIb, p. 1068).

The Composition of Solutions made by Dissolving Sodium in Aqueous Alcohol.—The composition of solutions prepared by dissolving sodium in aqueous ethanol or "absolute alcohol" may be computed somewhat similarly. The amount of water removed from the solution according to reaction (1) is equivalent to the hydroxide produced, so that at equilibrium $[H_2O] = c - [OH^-]$. Hence $K^\circ = [OH^-]/(b - [OH^-])(c - [OH^-])$. This again gives us a quadratic from which $[OH^-]/b$ can be found in terms of b , c , and K° . The results for ethanol containing initially 0, 0.2, and 1.0% of water by weight are given in Table 3. We have again used the limiting value of K° , but the range of base concentrations to which this applies now extends to 10M. From the Table it is evident that nearly all the base is present as ethoxide.

TABLE 3. *Percentage of total base present as hydroxide in solutions made by dissolving sodium in ethanol-water mixtures, at 25°.*

Wt. % water in solvent	Total base (%) present as hydroxide at			
	$b = 0.1M$	0.5M	1.0M	10M
0	0.0	0.0	0.0	0.0
0.2	0.7	0.7	0.7	0.4
1.0	3.4	3.3	3.2	1.9

Because the equilibrium (1) is rapidly established, sodium will not remove water from ethanol to the same extent as from an inert solvent; the water will be largely regenerated. If more sodium is present, it will react with this water, and so on up to the limit set by the solubilities of sodium ethoxide and hydroxide; but there will always be an equilibrium concentration of water. The final concentration of water can be estimated; it is given (see the preceding paragraph) by $[H_2O] = c - [OH^-]$, where $[OH^-]$ at various total base concentrations can be found from Table 3. We estimate that to remove only half the water from ethanol containing either 0.2% or 1% of water by weight, it is necessary to raise the total base concentration above 10M, *i.e.*, to add more than 230 g. of sodium per litre (incidentally this treatment will remove about half the ethanol as ethoxide). These conclusions apply to 25°. They suggest that treatment with sodium at room temperature would be a relatively inefficient means of finally drying ethanol. The efficacy of magnesium ethoxide for this purpose is accounted for by the insolubility of magnesium hydroxide in ethanol; hydroxide ions formed by equilibrium (1) are removed from solution, the equilibrium is disturbed so that more water reacts with ethoxide, and the water is progressively removed.

Relative Acid Strengths of Ethanol and Water.—The equilibrium constant K , and hence to a good approximation K' , is the ratio of the acid dissociation constant of water to that

of ethanol in any given solvent S, as may be seen by considering the equilibria $\text{EtOH} + \text{S} = \text{SH}^+ + \text{OEt}^-$ and $\text{H}_2\text{O} + \text{S} = \text{SH}^+ + \text{OH}^-$. In *ethanol*, we have found that K' at 25° is 0.5, so that the acid strengths of water and ethanol in this solvent are comparable, water being somewhat the weaker acid. In pure *water*, we find by extrapolation using the Figure that $\log_{10} K' = 0.8 (\pm 0.3)$; so that the acid strengths are again not greatly different, water being about 5 times the stronger acid. These relatively small differences in acid strength between water and ethanol are in accord with the view (cf. Bell, "Acids and Bases," Methuen, London, 1952, chap. 3) that the differences, amounting to a factor of the order of 10^4 , between the dissociation constants of neutral acids and bases measured in water and in ethanol can be attributed mainly to the differences in electrostatic forces, due to the difference of dielectric constant, rather than to a difference in the intrinsic acid strengths of the two solvents.

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