chain length is chiefly determined by the variation of the value of $\sqrt{\text{cmc}}$.

The densities of the magnesium alkane sulfonate solutions did not show any abrupt deviation of trend within the range of cmc. To the contrary, some of the densities in this region are remarkably linear. The solubilities show the same general behavior as the sodium salts,[17] but the increase in solubility is much more abrupt at the Krafft point.

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Infrared Absorption Study of Hydrogen Bonding Equilibria

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A study has been made of hydrogen-bonding equilibria using the infrared absorption due to the unassociated hydroxyl group. Sterically unhindered molecules associate in polymeric complexes. Agreement between theory and experiment obtained by the use of two dissociation equilibria constants, one for the dissociation of dimeric complexes and one for the dissociation of higher order complexes is better than that obtained by the single dissociation equilibrium constant scheme of Kempter and Mecke. These constants have been evaluated for a series of simple alcohols and phenols. If a phenol has one ortho position occupied by a large substituent such as a *t*-butyl group it will be sterically hindered and will associate almost entirely in dimeric complexes. The equilibrium constants for several such partially hindered phenols have been evaluated. Hydrogen bonding occurs between hydroxylated materials and proton-acceptor compounds. Equilibrium constants have been evaluated for the systems of benzyl alcohol and methyl ethyl ketone and of benzyl alcohol and 1,4-dioxane.

The present report is of some studies of the equilibrium of hydroxylated materials between the free or unassociated state and the hydrogen-bonded or associated state. The data for this were obtained by infrared absorption measurements wherein the absorption due to the "free" hydroxyl group was correlated with the amount of unassociated material present. Fox and Martin[1] reported in 1937 some studies on phenol from which they concluded that at moderate concentrations an equilibrium is set up between single and double (associated) phenol molecules. More recently Kempter and Mecke[2] examined phenol using the second overtone of the free hydroxyl stretching frequency. They assumed that complexes of all orders were possible and that all the equilibrium coefficients for the dissociation of complexes were the same, and their data appeared to check the theory satisfactorily. In the present work it was found that better agreement between theory and experiment was obtained if two equilibrium coefficients were used: one for the dissociation of the dimer complexes, and one which was applicable to the dissociation of the higher order complexes. It was found that the association of the partially hindered phenols is almost entirely dimer in nature. In addition, the association between benzyl alcohol and methyl ethyl ketone and between benzyl alcohol and dioxane has been studied.

Equilibrium Equations

Case of a Single Equilibrium Constant.—Kempter and Mecke[2] considered equilibria of the type

$$(\mathrm{ROH})_n + \mathrm{ROH} \rightleftarrows (\mathrm{ROH})_{n+1}$$

where the subscripts n and $n + 1$ refer to complexes of the nth and $n + 1$th order. They assumed that the dissociation constants were equal for all orders of complexes and hence derived the equation

$$K_c = \alpha C/(1 - \sqrt{\alpha}) \qquad (1)$$

where K_c is the general dissociation constant applicable to each order complex, α is the fraction of hydroxylated molecules which are unassociated, and C is the concentration in moles per liter of hydroxylated material. When they plotted αC *vs.* $\sqrt{\alpha}$ for phenol, Kempter and Mecke obtained a straight line plot from which they concluded that agreement between their theory and experiment was satisfactory. It has not been possible to obtain agreement between our data and this simple theory and this led to a modification of the theory as given in the next section.

Case of Two Equilibrium Constants.—Here the assumption of equality of all dissociation constants is rejected. Instead we use a distinct constant K_1 for the dissociation of dimer complexes and a general constant K_c for all others, *i.e.*, $K_2 = K_3 = K_4 \ldots . = K_c$. This procedure is based on evidence from three different considerations: (a) the shape and wave length maxima of the association bands at low concentration, (b) the disagreement with data encountered using the simpler scheme, and (c) the evidence that the potential energy in the formation of a dimer complex is considerably less than the potential energy change when an n-fold complex adds a member to become an $n + 1$-fold complex. A discussion of these points will be given later.

Utilization of the equilibrium conditions between the various orders of complexes leads to the relation

$$\alpha_n = n\alpha \frac{K_c}{K_1}\left\{\frac{\alpha C}{K_c}\right\}^{n-1} \qquad (2)$$

where α_n refers to the fraction of hydroxylated molecules bound in complexes of the $n + 1$th order. With the use of the relation $\Sigma\alpha_n = 1$ one may then derive the expression for K_c, namely

$$K_c = \frac{\alpha C}{2(K_1 - \bar{K}_1)}\left\{2K_1 - \frac{\bar{K}_1}{2} + \sqrt{2K_1\bar{K}_1 + \frac{\bar{K}_1^2}{4}}\right\} \qquad (3)$$

where $\bar{K}_1 = 2\alpha^2C/(1 - \alpha)$. To evaluate K_c from Eq. 3 one must first evaluate K_1. It may be shown from operations on Eq. 3 that lim $\alpha^2C/(1 - \alpha) = K_1/2$ as $C \rightarrow 0$. Therefore, K_1 may be evaluated by plotting $\bar{K}_1 = 2\alpha^2C/(1 - \alpha)$ *versus* C and extrapolating to zero concentration.

Experimental Details

All infrared absorption data were obtained on a Perkin-Elmer Model 12B spectrometer equipped with a LiF prism. The transmission measurements were made manually using a null system previously described.[3] Three different cell thicknesses were used. For the study of association between hydroxylated molecules and other materials such as ketones, etc., a cell of 1.4 cm. thickness was used. For the studies on alcohols a cell of 0.036" thickness was used. For the phenols a cell of 0.006" thickness was used. The difference in the latter two cell thicknesses is a result of the wide difference of extinction coefficients for the alcohols as a

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[1] J. J. Fox and A. E. Martin, *Proc. Roy. Soc. (London)*, **162**, 419 (1937).

[2] H. Kempter and R. Mecke, *Z. physik. Chem.*, **46**, 229 (1941).

[3] N. D. Coggeshall and E. L. Saier, *J. Applied Physics*, **17**, 450 (1946).

class and for the phenols as a class. The latter two cells were of a design previously described.[4]

The compounds studied were all of C.P. grade and from commercial sources except for the partially hindered phenols. These were supplied by Dr. R. S. Bowman and had been subjected to repeated purifications by recrystallization. In all cases the equilibria were studied in carbon tetrachloride solution.

As the absorption band of the associated hydroxyl group is broad, it might be expected to contribute some absorption at the free hydroxyl band. In order to test this, the data of Fig. 1 were obtained. If the association band (centering between 2.90 and 3.00 μ) is extrapolated through the base of the free hydroxyl band (occurring at 2.77 μ) it provides the contribution from the association band. The extrapolation cannot be done by assuming symmetry of the association band about a center as the long wave length side is raised through contributions from the C–H stretching vibrations. In fact, the extrapolation cannot be done with known precision. If it is done by extending the association band linearly as shown by the dashed line in curve f of Fig. 1, it is obvious that the contribution is at most very small. In view of this, no corrections for such possible contributions were made.

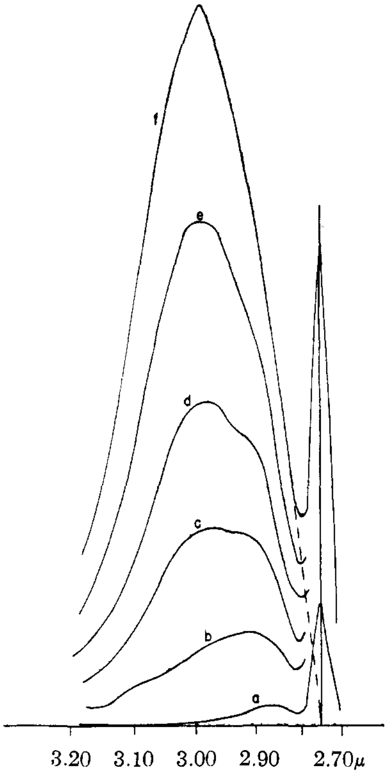

Fig. 1.—Plot of optical density *versus* wave length for benzyl alcohol in carbon tetrachloride solution at (a) 0.0486 mole/liter, (b) 0.0972 mole/liter, (c) 0.155 mole/liter, (d) 0.194 mole/liter, (e) 0.243 mole/liter and (f) 0.278 mole/liter (from reference 5).

All data used in the equilibrium calculations for any one compound were obtained in the same cell. The absorption measurements were all carried out in an air conditioned room in which the temperature was held constant to about ±2°F. It is important that such measurements be made at controlled temperatures as the population of the complexes is affected by temperature. This may be seen in Fig. 2 which shows the association band of a 0.24 m./l. solution of benzyl alcohol over a range of temperatures from 11 to 62°. It is obvious that this temperature increase destroys most of the complexes.

An experimental difficulty generally present in such measurements is the result of the water vapor in the air in the neighborhood of the absorption cells. The hydroxyl absorption of the water vapor occurs close to that of the hydroxylated materials studied. If the water vapor concentration in this region is constant, the effect will cancel out in the ratio of the incident and transmittal energies. If it is varying, noticeable errors may be introduced. To eliminate this, the ratios were evaluated in duplicate.

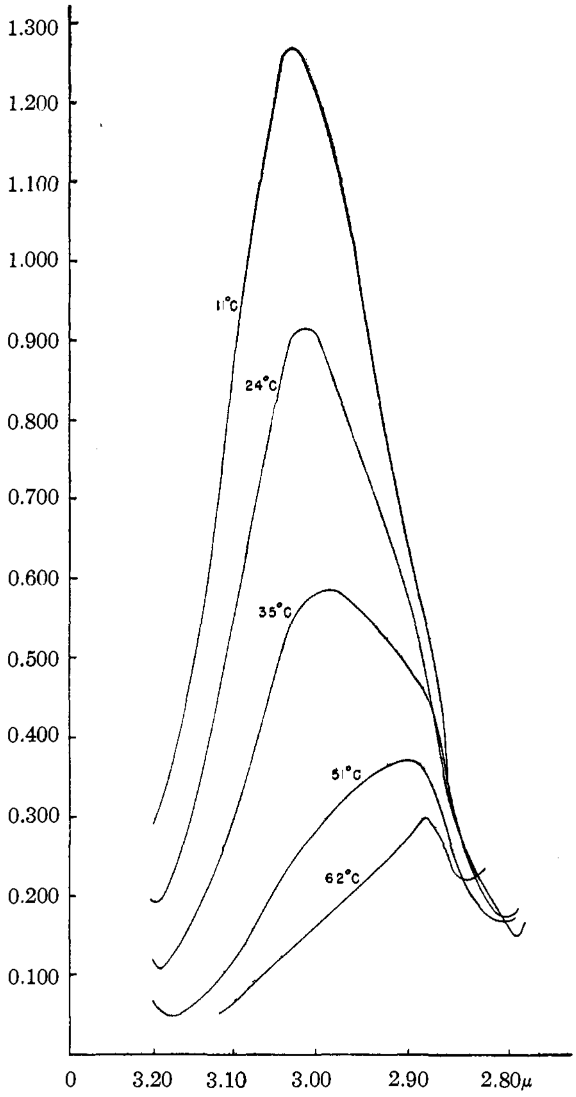

Fig. 2.—Plot of optical density *versus* wave length through the hydroxyl absorption region for a solution of 0.24 mole/liter of benzyl alcohol in carbon tetrachloride for different temperatures in the 11–61° range.

Compounds Exhibiting Polymeric Association

In this class fall all of the alcohols and the unhindered phenols examined. These were *n*-propyl, *n*-butyl, *t*-butyl, benzyl and *n*-octyl alcohol and phenol and *p*-*t*-butylphenol. The data for these were first examined by the single constant scheme of Kempter and Mecke by the tests described below.

Beer's law of absorption for the hydroxyl absorption band is obeyed for sufficiently dilute solutions. Hence log $I_0/I = D = hCl$ where I_0 and I are incident and transmitted energy rates, D is the optical density, h is the extinction coefficient and l is the length of the cell. Since constant cell thicknesses were used, one may write $D = gC$ where $g =$

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[4] N. D. Coggeshall, *Rev. Sci. Instruments*, **17**, 343 (1946).

hl. With this notation we may calculate α for a solution allowing bonding by the relation $\alpha = D/gC$. We may evaluate g by plotting D/C *versus* C and extrapolating to zero concentration.

(a) **D *versus* $\sqrt{D/C}$ Plots.**—This is equivalent to plotting αC *vs.* $\sqrt{\alpha}$ which should, according to the simpler theory, provide a straight line. In Fig. 3 may be seen such a curve for phenol. As this curve is typical, others will not be shown. Each was observed to give an approximate straight line plot except for a dropping away of the points in the higher $\sqrt{D/C}$ region and a general concavity to the $\sqrt{D/C}$ axis. Neither of these effects should be present if the single dissociation constant theory were correct.

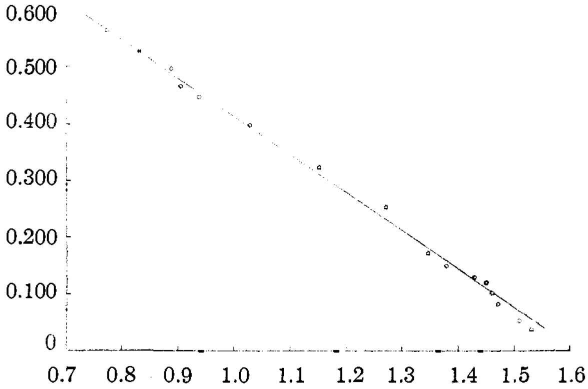

Fig. 3.—Plot of D *versus* $\sqrt{D/C}$ for phenol.

(b) **Direct Evaluation of K_c.**—From above K_c may be obtained directly through Eq. 1 over a series of values of α. In Table I are given the values of K_c calculated for a range of concentrations for n-octyl alcohol, n-butyl alcohol and phenol.

TABLE I

VALUES OF K_c CALCULATED FOR VARIOUS VALUES OF C IN (MOLES/LITER)

n-Octyl alcohol		n-Propyl alcohol		Phenol	
C	K_c	C	K_c	C	K_c
0.101	0.680	0.0820	0.672	0.0569	0.690
.202	.610	.154	.630	.158	.549
.244	.560	.205	.497	.237	.523
.303	.510	.410	.472	.474	.485
.504	.493	.615	.443	.758	.463
.576	.460	.714	.432	.948	.456

In each case K_c varied by about 35% over these concentrations. This is contrary to the predictions of the single constant theory. Similar variations of K_c were also observed for the other materials exhibiting polymeric association.

(c) **Evaluation of K_c Through Pairs.**—By proper operations both K_c and g may be algebraically derived from pairs of data points. When this is done there is found to be a certain amount of scattering in the values of K_c and g which is not correlated with the pairs of points used. Furthermore, this procedure yields values of g which are always larger than the experimentally determined values by approximately 10%.

Résumé for Single Dissociation Constant Calculations.—We have thus seen that each of the three methods of correlating data with the theory for the single dissociation constant scheme produces discrepancies which are systematic and cannot be ascribed to experimental error. These discrepancies form one basis for rejecting the single constant scheme.

In Fig. 1 it may be observed that the wave length of maximum absorption for the association band varies with concentration. At the lower concentrations it is near 2.90 μ and for the higher concentrations it is near 3.00 μ. The bands for the intermediate concentrations have the definite appearance of superposition of two such maxima. We must ascribe the lower wave length band to dimer association and the longer wave length band to the higher order complexes. The wave length shift of the perturbed hydroxyl absorption is dependent on the energy of association, the more tightly bound complexes giving rise to greater wave length shifts. We thus have an evident difference of potential energy for molecules in dimer and higher order complexes. This in turn indicates the necessity of considering two dissociation coefficients: one for the dimer complexes, and one for the higher order complexes.

Recent calculations,[5] employing a linear polymer model of association, have shown that the energy released on forming a dimer is considerably smaller than the energy released on increasing the order of a higher order complex by one. The latter is essentially independent of n for $n > 3$. This is a further indication of the necessity of rejecting a single equilibrium constant.

Calculation of Two Equilibrium Constants.—We have seen earlier that K_1 may be evaluated by extrapolating $2\alpha^2C/(1 - \alpha)$ to zero concentration. The manner of doing this may be seen from Fig. 4 which shows the extrapolation for K_1 for n-butyl alcohol. It is seen that the points scatter rather badly in the low concentration region. This is a consequence of the small $(1 - \alpha)$ term in the denominator and it is a fundamental difficulty in this method of evaluating K_1. In each case K_1 was determined by drawing a "best curve" through the points, being guided insofar as reasonable by the behavior as it receded from the higher to lower values of the concentration.

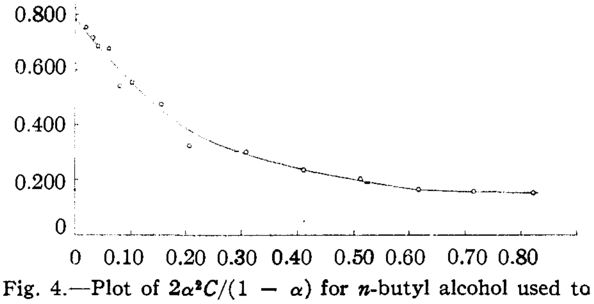

Fig. 4.—Plot of $2\alpha^2C/(1 - \alpha)$ for n-butyl alcohol used to determine K_1.

With the extrapolated values of K_1, values of K_c were calculated for each concentration through the use of Eq. 3. In each case there was a certain

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(5) N. D. Coggeshall, *J. Chem. Phys.*, **18**, 978 (1950).

amount of scattering in the calculated K_c values. These showed no systematic trend with concentration and the discrepancies are ascribed to limitations in precision of the data and of the extrapolated values of K_1. The expression for K_c involves

$$(K_1 - \bar{K}_1) = K_1 - 2\alpha^2C/(1 - \alpha)$$

which is both small and of doubtful reliability for low values of concentration. In view of this the values of K_c calculated for low concentrations were not used in the averages. In Table II may be seen the typical scattering occurring at the higher concentrations.

TABLE II

K_c CALCULATED FOR *n*-OCTYL ALCOHOL

C, m./l.	K_c	*C*, m./l.	K_c
0.244	0.36	0.452	0.35
.303	.33	.504	.36
.352	.33	.576	.34
.403	.36		

In Table III may be seen the extrapolated values of K_1 and the average value of K_c calculated for each of the compounds exhibiting polymeric association.

TABLE III

EXTRAPOLATED AND CALCULATED VALUES OF K_1 AND K_c

Material	K_1	K_c
n-Propyl alcohol	0.89	0.33
Benzyl alcohol	.80	.33
n-Octyl alcohol	.77	.35
n-Butyl alcohol	.78	.33
t-Butyl alcohol	.58	.40
p-*t*-Butylphenol	.58	.34
Phenol	.72	.34

The data of Table III demonstrate that the equilibrium constants are all of the same order of magnitude and apparently are roughly independent of molecular weight and structure.

In resumé of polymeric association it must be concluded that at least two equilibrium constants are necessary to get satisfactory agreement between theory and experiment.

Compounds Subject to Dimeric Equilibrium

Earlier studies on substituted phenols have shown that large ortho substituents sterically hinder hydrogen-bonding.[6] Phenols with both ortho positions thus substituted do not form complexes. Phenols with one ortho position thus occupied, otherwise known as partially hindered phenols, are known to form weaker bonds than the simple alcohols and phenols. In view of the molecular geometry it would be expected that the partially hindered phenols would associate in dimer form but would not form the polymeric complexes. This may be determined by examination of the term $2\alpha^2C/(1 - \alpha)$ over a range of concentrations sufficient for polymeric equilibrium. If this term is essentially constant it may be shown to be a necessary and sufficient condition for dimeric equilibrium.

In Table IV may be seen the values of $2\alpha^2C/(1 - \alpha)$ for various concentrations for four partially hindered phenols. The values were not used for the lower concentrations, as they are not so reliable because of the $(1 - \alpha)$ term which is quite small and which appears in the denominator.

TABLE IV

VALUES OF $K = 2\alpha^2C/(1 - \alpha)$ FOR PARTIALLY HINDERED PHENOLS FOR VARIOUS CONCENTRATIONS

2,4-Di-*t*-butylphenol *C*, m./l.	*K*	*o*-*t*-Butylphenol *C*, m./l.	*K*	2-*t*-Bu-4-methylphenol *C*, m./l.	*K*	*o*-*s*-Butylphenol *C*, m./l.	*K*
0.200	1.00	0.102	0.62	0.102	1.26	0.201	0.97
.250	1.06	.204	.67	.305	1.47	.315	.81
.333	0.88	.409	.67	.406	1.49	.402	.81
.500	1.06	.545	.62	.508	1.43	.496	.72
.666	0.96	.614	.68	.609	1.26	.603	.63
.750	.94	.700	.69	.678	1.37	.690	.59
1.000	.85	.818	.63	.812	1.34	.801	.56
K(av) = 0.96		*K*(av) = 0.65		*K*(av) = 1.37		*K*(av) = 0.73	

It will be noticed that there is considerable scattering of the *K* values but, except for *o*-*s*-butylphenol, there is no definite trend with concentration. The scattering is ascribed to limitations of experimental measurements. Excepting *o*-*s*-butylphenol, it may be concluded that the association of the partially hindered phenols is dimeric in nature.

The variation of *K* with concentration for *o*-*s*-butylphenol indicates that it is not so effectively hindered and that polymeric equilibrium is possible. With this in mind, the methods of the earlier section were used to calculate the values: $K_1 = 1.00$ and $K_c = 1.39$ for this material..

Association Between Unlike Species

Association may occur between hydroxylated materials and proton-acceptor materials. Evidence for this may be seen in Fig. 5. This gives the recorded energy traces for three different solutions, vertically displaced for clarity. Curve A is for 0.015 ml. of ethyl alcohol and the free hydroxyl absorption band may be seen centering on the left-hand dashed line. Curve B is for the same concentrationg of ethyl alcohol to which has been added 0.235 m./l. of acetone. The energy minimum centering on the center dashed line is due to hydroxyl groups which are in association with the acetone. The other minima seen for this curve are due to the acetone itself. Curve C is for the same concentration of ethyl alcohol to which has been added 0.235 m./l. of 1,4-dioxane. Here the energy minimum centering on the right-hand dashed line is due to hydroxyls in association with the dioxane. The other minima are due to the dioxane.

In these studies quantitative data were obtained for benzyl alcohol in the presence of a methyl ethyl ketone and in the presence of 1,4-dioxane. Each of the latter two compounds have appreciable absorption at the hydroxyl absorption band. Since they are used in concentrations considerably in excess of the benzyl alcohol, it is necessary to accurately evaluate these contributions. This was done by running a series of solutions containing these materials separately.

In order to eliminate the effect of association between alcohol molecules, the latter concentration was held at 0.002 m./l. and the dioxane or ketone concentrations were varied. With this arrange-

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(6) N. D. Coggeshall, THIS JOURNAL, **69**, 1620 (1947).

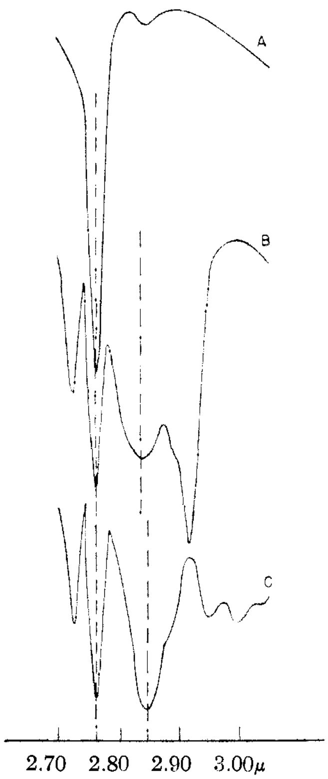

Fig. 5.—Automatic infrared recordings in the 2.7–3.0 μ region showing spectra of (A) 0.015 mole/liter of ethyl alcohol in carbon tetrachloride, (B) 0.015 mole/liter of ethyl alcohol plus 0.235 mole/liter of acetone in carbon tetrachloride and (C) 0.015 mole/liter of ethyl alcohol plus 0.235 mole/liter of 1,4-dioxane in carbon tetrachloride.

ment only binary association involving the alcohol is expected. This is expressed by the equation

$$\alpha\{X - (1 - \alpha)C\} = K(1 - \alpha)$$

where α and C have the same meanings as before, X is the concentration of proton-acceptor material and K is the dissociation constant for the complexes between hydroxylated and proton-acceptor molecules. Experimentally it is found that for reasonable degrees of association $X \gg C$ so we have

$$\alpha X = K(1 - \alpha)$$

from which K may readily be determined.

In Table V may be seen the values of K calculated for the system of benzyl alcohol and methyl ethyl ketone.

TABLE V

DISSOCIATION CONSTANT K FOR BENZYL ALCOHOL, METHYL ETHYL KETONE SYSTEM

Concn. of methyl ethyl ketone, m./l.	K	Concn. of methyl ethyl ketone, m./l.	K
0.03	0.24	0.18	0.18
.06	.26	.21	.15
.09	.30	.24	.13
.12	.26	.27	.11
.15	.25		

It may be seen that the values of K scatter within a definite range for concentrations of methyl ethyl ketone up to 0.15 m./l. and then drop sharply for higher values. The first five values yielded an average of $K = 0.26$. It is believed that the value of $K = 0.30$ among the first five values is in error as it is erratically displaced when a plot of the data is made.

It is assumed that the decrease of the calculated value of K for the larger concentrations of proton-acceptor material is due to solvent effects. A similar behavior was also observed for the benzyl alcohol, 1,4-dioxane system. For this system the lower concentration range of proton-acceptor material yielded an average value for the dissociation value of $K = 0.20$.

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