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Investigation of the Association of Alcohols and Phenols by the NMR Method

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The review discusses and analyses the literature on the study of the association of alcohols and phenols by the NMR method. The methods for the determination of the equilibrium constants and heats and entropies of formation of the association complexes of the above substances in both inert and basic solvents are described for equilibria of different types.
The polar and steric effects of the substituents in alcohols and phenols on the thermodynamic functions for the formation of self-association complexes and also of association complexes with polar molecules has been analysed.
The bibliography comprises 151 references.

CONTENTS

I. Introduction 347
II. Self association 348
III. Association 351

I. INTRODUCTION

In recent years the nuclear magnetic resonance (NMR) method has been widely used in structural investigations and also in the study of problems such as isomerism, tautomeric equilibria, reaction rates, and others[1-3]. An important application of the method is also the study of intermolecular interaction and in particular association processes in hydrogen-bonded systems. The wide use of NMR for this purpose is due to its many advantages compared with the traditional procedures for the investigation of hydrogen bonds, for examples infrared spectroscopy. The advantages include primarily the relative simplicity of the NMR spectra and a fairly high sensitivity of the method, which allows the observation of shifts due to the formation of hydrogen bonds even in the case of relatively weak interactions. The availability of a frequency scale for NMR measurements permits the determination of the lifetime of the association complex formed by hydrogen bonding or the limits of existence of the complex. When strong intramolecular hydrogen bonds are formed, the band due to the OH group in infrared spectra is frequently so diffuse that it is very difficult to observe. In contrast, the detection of such bonds by NMR spectroscopy does not present difficulties, since the NMR signals in liquid specimens and in solutions are as a rule fairly narrow. The NMR method permits the investigation of aqueous solutions, the study of which by infrared spectroscopy is difficult due to the opacity of water as a solvent in the relevant regions of the infrared spectrum.

Numerous studies on association processes using NMR undertaken after the initial investigations[4,5] showed that a general property of systems with intermolecular hydrogen bonds is a parallel shift of the proton signal of the OH group with temperature and with dilution. Studies on the concentration and temperature dependence of the NMR signal yielded extensive data on the characteristics of hydrogen bonds, led to the determination of the degree of

association in various systems, and made it possible to establish the effects of polar and steric factors in molecules on the thermodynamic characteristics of the formation of association complexes.

The problems associated with the application of the NMR method in the study of hydrogen-bonded systems are discussed in a number of monographs and reviews[1-3,8-12]. However, most of them do not deal with the many studies carried out in recent years.

This review presents a discussion of the results obtained in studies by NMR of the association of alcohols and phenols. In this connection the methods for the determination of the equilibrium constants and other thermodynamic properties of the formation of association complexes are briefly described. The self-association processes of alcohols and phenols in inert solvents and their association with bases are discussed.

The review is not concerned with problems of the hydrogen bond theory, which are discussed at a contemporary level in a number of publications[13-16] or with the nature of and methods for the calculation of chemical shifts accompanying hydrogen bond formation[13,17-24].

II. SELF-ASSOCIATION

1. Self-association Equilibrium Constants

In pure liquids and also in solutions of many substances in an inert solvent, there is a possibility of the formation of association complexes of molecules of one kind. In contrast to other spectroscopic methods[1], in the NMR spectrum the proton involved in the hydrogen bond gives rise to one averaged signal, the chemical shift of which corresponds to a mean screening for all the existing states when account is taken of their statistical weight. This is because the frequency with which hydrogen bonds are formed and dissociated exceeds by several powers of ten the frequency at which resonance absorption by protons is usually observed[25,26]. This property is responsible for certain unusual features in the method used to find the association parameters—equilibrium constants and thermodynamic functions—from NMR data.

Consider the monomer—n-mer equilibrium[2,27,28]:

$$nA \rightleftarrows (A)n\,. \qquad (I.1)$$

We shall denote by A_0, C and S the initial concentration of substance A, the equilibrium concentration of the association complex, and the initial concentration of the inert solvent (with $A_0 + S = 1$), and by n the number of monomeric molecules entering into the composition of the self-association complexes. Then the equilibrium constant expressed in mole fractions is

$$K = \frac{c[1-(n-1)c]^{n-1}}{(A_0 - nc)^n}\,. \qquad (I.2)$$

The chemical shift of the average signal τ in cyclic association is defined by the expression

$$\tau = \frac{nc}{A_0}\tau_n + \frac{(A_0 - nc)}{A_0}\tau_m = n\alpha\Delta\tau + \tau_m, \qquad (I.3)$$

and in linear association by the expression

$$\tau = \frac{(n-1)c}{A_0}\tau_n + \frac{A_0-(n-1)c}{A_0}\tau_m = \alpha(n-1)\cdot\Delta\tau + \tau_m, \qquad (I.3^a)$$

where τ_m and τ_n are the chemical shifts of the proton in the free and hydrogen-bonded states, τ is the observed chemical shift of the proton, $\alpha = C/A_0$ the degree of self-association, and $\Delta\tau = \tau_n - \tau_m$.

It is clear from Eqns. (I.2), I.3), and (I.3a) that, when τ_m, τ_n, and the initial concentration A_0 are known, it is possible to find the degree of association α and the equilibrium constant K for the formation of the association complexes. However, the determination of exact values of τ_m and τ_n is a complex problem. The difficulties in the determination of the first chemical shift are associated with the inadequate sensitivity of modern NMR apparatus, which precludes measurements at very low concentrations where the existence of the solute in the monomeric state is most likely. Moreover, even at the lowest concentration there is no certainty that the given substance is entirely present as the monomer (this applies, for example, to carboxylic acids). The chemical shift τ_n cannot be determined accurately because of the presence in concentrated solutions of association complexes of species with a degree of polymerisation different than that of n-meric molecules and also because of the possible presence of unassociated molecules. Therefore various approximations are usually employed in the determination of association parameters from NMR data.

Let us consider the variation of the chemical shift at low concentrations of the solute ($A_0 \rightarrow 0$). At the point $A_0 = 0$ the slope of the extrapolated chemical shift–concentration curve is defined by the following expressions: for a cyclic association complex,

$$\left(\frac{d\tau}{dA_0}\right)_{A_0\to 0} = n\,\Delta\tau\left(\frac{d\alpha}{dA_0}\right)_{A_0\to 0}, \qquad (I.4)$$

and for a linear association complex,

$$\left(\frac{d\tau}{dA_0}\right)_{A_0\to 0} = (n-1)\,\Delta\tau\left(\frac{d\alpha}{dA_0}\right)_{A_0\to 0} \qquad (I.4^a)$$

The quantity $(d\alpha/dA_0)_{A_0\to 0}$ is found by differentiating Eqn. (I.2) with respect to A_0. It has been shown[27-29] that only for monomer–dimer equilibrium ($n = 2$) is $(d\alpha/dA_0)_{A_0\to 0}$ and hence the slope of the chemical shift–concentration curve non-zero. Then

$$\left(\frac{d\alpha}{dA_0}\right)_{A_0\to 0} = K_2\,.$$

Examination of the variation of the chemical shift at very low concentrations ($A_0 \rightarrow 0$) does not eliminate the difficulty in the determination of the equilibrium constant because of the complexity of the accurate measurement of $\Delta\tau$,[29] although it does make it possible to establish the type of association. However, it should be noted that a non-zero slope of the concentration variation of the chemical shift at low concentrations is observed also for the monomer + $(n-1)$-mer $\rightleftarrows$ n-mer association[28].

At moderate and high concentrations of the solute, in contrast to the region of low concentrations, the concentration variation of the chemical shift deviates from linearity even in the monomer–dimer equilibrium, as follows from the simultaneous solution of Eqns. (I.2) and (I.3) or (I.2) and (I.3a). Moreover, the deviation of the relation from linearity also occurs due to the presence in solution of association complexes of higher orders than at low concentrations.

For simplicity, it is usually assumed that even at high concentrations only one type of association occurs in solution. In this approximation simultaneous solution of Eqns. (I.2) and (I.3) with $|\tau_m| > |\tau_n|$ leads to the expression[12]

$$\frac{\tau_m - \tau}{\tau_m - \tau_n} = nKA_0^{n-1}\left(\frac{\tau - \tau_n}{\tau_m - \tau_n}\right)^n. \qquad (I.5)$$

Since

$$\frac{\tau_m-\tau}{\tau_m-\tau_n}+\frac{\tau-\tau_n}{\tau_m-\tau_n}=1,$$

Eqn. (I.5) can be reduced to the form

$$\sqrt[n]{\frac{\tau_m-\tau}{A_0^{n-1}}}=\sqrt[n]{n\ K\ (\tau_m-\tau_n)}-\sqrt[n]{n\ K\ (\tau_m-\tau_n)^{1-n}}\ (\tau_m-\tau) \tag{I.6}$$

or

$$(\tau-\tau_n)^n A_0^{n-1}=(\tau_m-\tau_n)^n/n\ K-(\tau_m-\tau_n)^{n-1}\ (\tau-\tau_n)/n\ K\ . \tag{I.6a}$$

Eqns. (I.6) and (I.6a) permit the graphical determination of the association order n, $\Delta\tau$, and the equilibrium constant. The accuracy of the determination of the last two quantities by this method depends entirely on the accuracy of the determination of the chemical shift of the monomer τ_m or the chemical shift of the n-mer τ_n.

The dependence of the chemical shift on the logarithm of the solute concentration usually has a point of inflection[12,30-32], the position of which is determined by the degree of association. Indeed, knowing the approximate values of τ_m and τ_n and taking the second derivative of the logarithmic form of Eqn. (I.5) with respect to the logarithm of the concentration, we find that at the point of inflection

$$n=\left(\frac{\tau_p-\tau_n}{\tau_m-\tau_p}\right)^2$$

where n is the integral value of the association order and τ_p the chemical shift at the point of inflection. Combination of Eqn. (I.5) with its logarithmic form and the derivative of the latter with respect to the logarithm of the concentrations yields

$$\tau_m=\tau_p+\frac{1}{\sqrt{n}-1}\left(\frac{d\tau}{d\ln A_0}\right)_p,$$

$$\tau_n=\tau_p-\frac{\sqrt{n}}{\sqrt{n}-1}\left(\frac{d\tau}{d\ln A_0}\right)_p, \tag{I.7}$$

$$\ln K=(n-1)(-\ln A_0)_p-\frac{n+2}{2}\ln n.$$

The method described permits the determination of the association order from approximate values of τ_m and τ_n and also the calculation of the equilibrium constant and more accurate values of τ_m and τ_n.

If the point of inflection in the relation between the chemical shift and the logarithm of the concentration is outside the limits of measured values of τ, the association parameters are usually determined by comparing the experimental variation of the chemical shift τ with that calculated from the modified Eqn. (I.5) for different n.[30,32] It is noteworthy that this method is far from accurate and frequently yields markedly different results for the same systems[33].

The above methods for the determination of association parameters make it possible to find fairly reliably only the association order n, while the accuracy of the calculated equilibrium constant is lower. The reliability of the calculated equilibrium constants may be significantly enhanced using, for example, the linearity of the dependence of the chemical shift on the degree of association α. By determining α from Eqn. (I.2) and substituting it in Eqn. (I.3), we find that

$$\tau=n\,\alpha(K,A_0)\,\Delta\tau+\tau_m\,. \tag{I.8}$$

By varying K successively in the function $\alpha(K,A_0)$, we find its value which gives the maximum correlation coefficient of the linear equation (I.8). This method has the advantage that it is not necessary to know τ_m and $\Delta\tau$ in order to find K. It was used in our determination[34] of the monomer–dimer equilibrium constants in the study of the association of dihydric and trihydric phenols.

In a number of investigations it has been shown[35-37] that the quantities τ_m and $\Delta\tau$ are almost independent of temperature. This made it possible to determine the heat of formation of the dimeric association complexes (ΔH) from the variation of the slope of the chemical shift–concentration curve with temperature using Eqn. (I.4):

$$\ln\left(\frac{d\tau}{dA_0}\right)_{A_0\to 0}=-\frac{\Delta H}{RT}+\text{const.} \tag{I.9}$$

In the monomer–n-mer equilibrium the heat of formation of the association complexes is determined either from the temperature variation of the point of inflection in the relation between the chemical shift and the logarithm of the concentration [Eqn. (I.7)] or from the temperature variation of the chemical shift at a given concentration[33]. In this case combination of Eqns. (I.2) and (I.3) with the equation $RT\ln K=-\Delta H+\Delta ST$ leads to the expression

$$\ln\left(\frac{\tau_m-\tau}{(\tau-\tau_n)^n}\right)=-\frac{\Delta H}{RT}+\text{const.} \tag{I.10}$$

In the approximation discussed ΔH is determined by varying n in such a way that the maximum correlation coefficient of the linear equation (I.10) is obtained for the given τ_m and τ_n.

A significant disadvantate of the method described is the need for accurate values of τ_m and τ_n, which are almost impossible to determine from the temperature variation alone. There is more justification for the use of these quantities found from the concentration variation in combination with data on the temperature variation of the chemical shift at a given concentration in order to determine the effect of temperature on the equilibrium constant.

2. Alcohols

In the study of the self-association of aliphatic alcohols (methyl, ethyl, isopropyl, and t-butyl), it was found that the difference between the chemical shifts of the monomeric species and species associated to the maximum extent (the self-association shift $\Delta\tau$) is approximately constant and of the order of 5 p.p.m.[35,38] This shift is so large that, on maximum dilution, the signal of the OH proton is displaced towards stronger fields than those in which the signal of the CH_3 is located. However, despite the approximately equal values of $\Delta\tau$ for these alcohols, the degree of their self-association decreases appreciably on going from methyl to t-butyl alcohol[39,40].

The composition of the multimers formed in the self-association of aliphatic alcohols has been investigated in a number of studies. Thus, by comparing the results of the measurements of the concentration dependence of τ^{OH} for methyl and t-butyl alcohol with calculated data for the monomer–dimer, monomer–trimer, and monomer–tetramer equilibria, it was found[30,41] that methanol is present in solution mainly as tetrameric association complexes and t-butyl alcohol mainly as trimeric complexes. In contrast, the study of the concentration variation of τ^{OH} for ethanol in carbon tetrachloride at very high dilutions showed[42] that the association complexes of this alcohol are predominantly dimeric. This finding agrees with the results of an infrared spectroscopic study by the same investigators[43]. Assuming that aliphatic alcohols are present in solution as dimers, the heats of formation of the

association complex ΔH were determined[35] and were found to be very close to the values obtained by the infrared spectroscopic method[43]. The dimeric association of aliphatic alcohols is also indicated by other results[44].

A detailed study of the composition of the association complexes of the alcohols and their thermodynamic characteristics was made by Feeney and Walker[33]. Since the values of ΔH for the bond O–H...O are usually in the range between 3 and 6 kcal mole^{-1},[1] they calculated from the temperature variation of τ^{OH} for methyl, ethyl, and t-butyl alcohols the heats of formation of the linear and cyclic dimers, trimers, and tetramers. From the ΔH values thus obtained, only those in the range 3–6 kcal mole^{-1} were selected. The results led to the conclusion that methyl alcohol forms in solution both linear and cyclic tetramers. In ethanol both linear and cyclic trimers and tetramers are possible, while for t-butyl alcohol ΔH indicates the presence in the solution predominantly of cyclic trimers. In their investigation a number of critical remarks were made concerning the results obtained in earlier studies. Thus Feeney and Walker[33] believe that the method involving the comparison of experimental and calculated concentration variation for n-mers[30] cannot be used for an accurate determination of either the type or the parameters of association. This method can indicate the order of association predominating only at a particular concentration, which makes it difficult to compare the results obtained in different investigations. On the other hand, the conclusion arrived at by Becker et al.[42] that monomer–dimer equilibrium occurs in alcoholic solutions is doubtful, since their investigation was made at a very high dilution. At higher concentrations the existence of other types of n-mers is quite possible.

The formation of cyclic t-butyl alcohol trimers is explained[33–45] by steric hindrance of the t-butyl groups which prevents the linear association of the molecule. Moreover, the specific stability of the six-membered ring formed makes some contribution to this form of association. It is noteowrthy that Huyskens et al.[46] suggest also the existence of non-cyclic chains of associated molecules, in addition to the cyclic species, in t-butyl alcohol solutions.

The data examined show that the problem of the composition of the association complexes of aliphatic alcohols in solution is far from being finally resolved. One may suppose that the formation of hydrogen bonds in solution produces varying extents of intermolecular association. This is indicated by a number of data. Thus Vanthiel et al.[47] observed in the infrared spectrum of pure methyl alcohol at low temperatures a number of distinct bands, which they believe can be accounted for by the presence of different types of association complexes: dimeric, trimeric, tetrameric, and polymeric. Studies on dilute solutions of methyl alcohol at room temperature led to the same conclusion[48]. X-ray diffraction analysis of alcoholic solutions[49] showed that at low concentrations monomer–dimer equilibrium occurs, higher association complexes being formed on increasing the concentration.

The effect of the introduction of a halogen atom into the alkyl group of the alcohol on its self-association has been investigated in a number of studies. It has been shown that the degree of self-association diminishes in the series ethanol > monochloroethanol > dichloroethanol > trichloroethanol[50–52]. These data are confirmed by the results of the investigation of chlorinated ethanols by the infrared spectroscopic method[53]. A comparative study of ethanol and trifluoroethanol led to a similar conclusion[54]. The chemical shift of the OH proton in monomeric trifluoroethanol obtained by extrapolation to infinite dilution occurs in the region of lower fields than for ethanol itself, which is due to the greater electronegativity of the CF_3 group compared with CH_3. The lower slope of the concentration variation of τOH at infinite dilution of trifluoroethanol compared with ethanol indicates that the latter has the higher degree of association in solution.

Comparison of propyl, allyl, and propargyl alcohols showed that the presence of the double bond and even more so a triple bond increases the degree of self-association of the alcohol[39]. It is believed that the effect is due to the increased acidity of the OH proton and the decrease of steric hindrance in the series of alcohols propyl > allyl > propargyl.

There are some NMR data, mostly qualitative, on the degree of association and the nature of the multimers formed in different alcohols[55,56]. Since the slope of the concentration variation of τ^{OH} for 2-methoxyethanol is not zero, it was concluded that the monomer–linear dimer equilibrium occurs in the solution of this alcohol[33]. Similar association is proposed also for 3-ethylpentan-3-ol,[57] a number of but-3-en-1-ol derivatives, and phenylethyl alcohol[58].

As the concentration of diacetone alcohol in carbon tetrachloride or cyclohexane decreases, the OH proton is displaced towards stronger fields, i.e. the self-association complexes break down, but intramolecular hydrogen bonds between the hydroxyl proton and the carbonyl oxygen are maintained[54]. The presence of both inter- and intramolecular hydrogen bonds has also been noted for a number of diols[59–61] and substituted ethylene glycols[62], the formation of hydrogen bonds in the latter being strongly influenced by the steric properties of the adjacent groups.

The chemical shift of the OH proton in a number of substituted 2-hydroxybenzophenones is relatively insensitive to changes in concentration but is altered approximately by 10 Hz when the temperature is raised from −25° to +80°C.[63] This is evidence of the presence in the compounds investigated of strong intramolecular hydrogen bonds the formation of which has been suggested also for diastereoisomeric α- and β-aminoalcohols[64]. An unusual intramolecular hydrogen bond between the hydroxyl proton and the oxygen of the methoxy-group has been observed in the study of solutions of substituted benzyl alcohols[65].

An interesting effect of hydrogen bonds was observed by Oki and Iwamura[66], who showed that an intramolecular hydrogen bond exists between the hydroxyl proton and the ring π electrons in aryldimethylmethanol, this being confirmed also by infrared spectroscopic data[67]. The signal due to the OH proton in aryldimethylmethanol shifts towards stronger fields on dilution[66], which is evidence of self-association of this compound in solution, the monomer-dimer equilibrium constant of the ring-substituted aryldimethylmethanols varying linearly with Hammett's σ constants for the substituents. A similar intramolecular interaction between the OH proton and π electrons has also been observed[68] in allyldimethyl- and benzyldimethylmethanol; in addition, intermolecular association complexes exist in solutions of the above alcohols.

Comparison of the chemical shifts of the OH and SH protons in methanol and methanethiol in gaseous, liquid, and solid phases indicates a much higher stability of the association complexes of methanol compared with its thioanalogue.[69]. In view of the linear variation of τ^{SH} for ethanethiol[70], n-propanethiol, and phenylmethanethiol[71] with concentration in carbon tetrachloride, it was con-

cluded that monomer–dimer equilibrium occurs in their solutions. The degree of self-association of aliphatic mercaptans decreases from methanethiol to t-butanethiol [72,73], in accordance with the known polar and steric properties of the alkyl group. The slope of the linear relation between τ^{SH} and temperature decreases in the same sequence [74].

Magnetic screening of the OH proton in aliphatic hydroperoxides (from n-propyl to n-octyl peroxide) is lower than for the OH proton in alcohols; its magnitude is similar to the screening of the proton in the carboxy-group of aliphatic acids [75,76]. When hydroperoxides are dissolved in carbon tetrachloride, the signal of the OOH proton shifts towards stronger fields, which indicates the breakdown of the self-association complexes.

3. Phenols

In the early studies on phenols by the NMR method [13,29,77,78] considerable changes in τ^{OH} on dilution with an inert solvent were already observed. However, the degree of self-association of phenols in solution is lower than for alcohols, as can be seen, for example, from a comparison of the concentration variation of the chemical shifts τ^{OH} of phenol and benzylalcohol in carbon tetrachloride [39,40], but is higher than for aniline and particularly for thiophenol [79].

Much work has been done on the effect of various substituents in phenol on its self-association. There is reason to believe that the introduction of electronegative substituents in the *para*- and *meta*-positions of phenols lowers the degree of self-association [39,41], while electropositive substituents increase it [80].

The problem of the effect of *ortho*-substituents on the self-association of phenols was investigated in greater detail. This effect is determined both by the change in the steric accessibility of the phenolic hydroxyl and the formation of intramolecular hydrogen bonds. The introduction of alkyl substituents in the *ortho*-position of phenol lowers its degree of the self-association, as already shown in the early studies on *o*-cresol [39] and 2,6-dimethylphenol [80]. The effect of *ortho*-alkyl substituents on the degree of self-association can be readily illustrated by a comparison [81] of the concentration dependence of the chemical shifts of the hydroxyl protons of 2,6- and 3,5-dimethylphenols in an inert solvent. The slope of the concentration variation of τ^{OH} for the phenol with methyl groups in the *ortho*-positions is much lower than for the phenol with the same substituents in the *meta*-positions. A detailed study of the effect of *ortho*-alkyl substituents on the self-association of phenols has been made [28,82–84]. The overall data obtained in these investigations indicate that an increase in the bulk of the *ortho*-substituents entails a sharp decrease of the degree of self-association of phenols. In 2,6-di-t-butylphenol the bulk of the *ortho*-substituents is so great that it precludes the mutual approach of the hydroxy-groups of two molecules to a distance sufficient for the formation of a hydrogen bond. In inert solvents this phenol is present in the monomeric state and its τ^{OH} is independent of concentration. At low concentrations (less than 0.1 p.p.m.) intermolecular hydrogen bonds are not formed also in solutions of 2,6-dimethyl- and 2,6-di-isopropyl-phenols [84,85]. The chemical shift due to intermolecular hydrogen bonds of *ortho*-substituted phenols is well correlated with the shift of the OH stretching vibration frequency in the infrared spectrum [84]. The importance of the effect of steric screening of the OH groups on the self-association of phenols has also been emphasised by Brodskii et al. [34], who investigated the concentration variation of τ^{OH} for many substituted *ortho*- and *para*-dihydric phenols. *Para*-dihydric phenols with t-butyl groups in their *ortho*-positions do not undergo self-association, while *ortho*--dihydric and trihydric phenols with bridging $-CH_2-$ groups form dimeric intermolecular association complexes, the equilibrium constants and thermodynamic characteristics of which have been determined.

The introduction of a halogen atom in the *ortho*-position of phenol reduces its degree of self-association [40]. This is consistent with the decrease in the accessibility of the OH group and with the possibility of the formation of an intramolecular hydrogen bond. The heat of formation of the O–H...halogen bond is low, in agreement with Raman spectroscopic data [86]: it varies from 2.4 to 1.7 kcal mole^{-1} on going from *ortho*-chloro- to *ortho*-iodophenol [87]. ΔH for the formation of intermolecular association complexes diminishes in the same sequence [88]. A linear relation between τ^{OH} and the frequency shift of the OH stretching vibrations in infrared spectra has been found for many *ortho*-substituted phenols [89].

In contrast to *ortho*-halogenophenols, which tend to form both intra- and inter-molecular hydrogen bonds, certain *ortho*-substituted phenols form intramolecular hydrogen bonds which are so stable that the intermolecular association is not observed in their solutions. These include, in the first place, *ortho*-nitrobenzene, salicylaldehyde, methyl salicylate, and others [40,90–93]. A comparative study of the concentration dependence of τ^{OH} for *para*-, *meta*-, and *ortho*-nitrophenols showed [94] that the first two phenols, which have no intramolecular hydrogen bonds, form self-association complexes in solution, while the *ortho*-isomer is monomeric.

Data on the composition of the multimers of phenols in the monomer–multimer equilibria are contradictory. Thus a monomer–dimer equilibrium has been suggested [29,82,95,96] for various phenols. However, analysis of the concentration variation of τ^{OH} for many phenols led to the conclusion [30,92] that they are predominantly trimeric, while di-*ortho*-alkyl phenols are largely tetrameric [11]. Thiophenols exist in inert solvents exclusively as monomers and dimers [97].

III. ASSOCIATION

1. Equilibrium Constant for the Formation of Binary Association Complexes

When a substance A dissolves in a solvent B forming hydrogen bonds with A, association complexes with A and B are formed. On the assumption that the self-association of A may be neglected, the following equilibrium is established in the solute–solvent system in the case of binary association:

$$A + B \rightleftarrows AB. \qquad (II.1)$$

Its equilibrium constant is given by the expression:

$$K = \frac{\beta(1-\beta A_0)}{(1-\beta)(B_0-\beta A_0)}, \qquad (II.2)$$

where A_0 and B_0 are the initial mole fractions of the solute and the solvent ($A_0 + B_0 = 1$), $\beta = x/A_0$ is the degree of association of A with the solvent B, and x is the equilibrium concentration of the association complex AB.

The chemical shift of the proton of A which formed an association complex AB with the solvent B is given by the expression

$$\tau = \beta\,\Delta\tau + \tau_A \qquad \text{(II.3)}$$

where $\Delta\tau = \tau_{AB} - \tau_A$ and τ_A and τ_{AB} are the chemical shifts of the free substance A and A hydrogen-bonded to B.

The chemical shifts τ_A and τ_{AB} are usually determined[12,99-100] by extrapolating the concentration variation of the overall chemical shift to $B_0 \to 0$ and $A_0 \to 0$ respectively.

In the extreme case with $A_0 \to 0$, Eqns. (II.2) and (II.3) yield[27,101]

$$(\tau)_{A_0\to 0} = \frac{K}{1+K}\Delta\tau + \tau^A,$$
$$\left(\frac{d\tau}{dA_0}\right)_{A_0\to 0} = -\frac{K}{(1+K)^2}\Delta\tau. \qquad \text{(II.4)}$$

Simultaneous solution of Eqns. (II.4) permits the determination of τ_A, τ_{AB}, and K. An interesting method for determining these quantities has been proposed by Mathur and coworkers[102,103]. Substitution of Eqn. (II.2) in Eqn. (II.3) when $B_0 \gg A_0$ yields the linear equation (II.5); all the association parameters can be determined from the slopes and intercepts of the corresponding plots:

$$\frac{1}{\tau - \tau_A} = \frac{1}{K\,\Delta\tau B_0} + \frac{1}{\Delta\tau}. \qquad \text{(II.5)}$$

Somewhat modified expressions of this type were obtained in special cases in other investigations[82,104]. It is noteworthy that in the methods described the accuracy of the determination of the equilibrium constant and $\Delta\tau$ is fully determined by the reliability with which τ_A is found.

More accurate association parameters can be obtained by analysing the variation of the chemical shifts over a wide range of concentrations[105,106]. Indeed simultaneous solution of Eqns. (II.2) and (II.3) gives the expression

$$\tau = \frac{(1+K) - \sqrt{(1+K)^2 - 4A_0B_0K(1+K)}}{2A_0(1+K)}\Delta\tau + \tau_A. \qquad \text{(II.6)}$$

Hence it is clear that, by choosing different values of K, a value can be found such that the sum of the squares of the differences between the calculated and experimental shifts is a minimum. The use of approximate formulae[107] for the estimation of the initial value of K close to the optimum value permits a rapid and reliable determination of the association parameters. An algorithm for the solution of this problem on electronic computers has been developed on the basis of Eqns. (II.2) and (II.6).[108] Nevertheless, it is noteowrthy that the value of this method is somewhat reduced by the need to know accurately τ_A and $\Delta\tau$. This difficulty may be overcome if the condition for a minimum sum of squares of the deviations is replaced by the condition of a maximum correlation coefficient for the linear equation (II.6),[109] which amounts to the same thing for a linear system.

The presence of the inert solvent S in the system causes some displacement of equilibrium, which affects the equilibrium constant. In this case the variation of the chemical shift with concentration is given by the expression[27]:

$$\tau = \frac{(1+KP) - \sqrt{(1+KP)^2 - 4A_0B_0K(1+K)}}{2A_0(1+K)}\Delta\tau + \tau_A, \qquad \text{(II.7)}$$

where $P = 1 - S$ and S is the mole fraction of the inert solvent ($A_0 + B_0 + S = 1$). When $P = 1$, Eqn. (II.7) becomes identical with Eqn. (II.6).

If self-association of one of the components takes place in the solution as well as the association of A and B, the two types of equilibria compete, namely self-association described by Eqn. (I.1) and association described by Eqn. (II.1).[27,110] When self-association complexes A_2 and association complexes AB are formed simultaneously in the system under the condition $A_0 + B_0 = 1$, the equilibrium constants are given by the following relations:

$$K_{A_2} = \frac{\alpha[1 - A_0(\alpha+\beta)]}{A_0[1-(2\alpha+\beta)]^2},$$
$$K_{AB} = \frac{\beta[1 - A_0(\alpha+\beta)]}{[1-(2\alpha+\beta)][B_0 - A_0\beta]}, \qquad \text{(II.8)}$$

where $\alpha = c/A_0$ and $\beta = x/A_0$ are the degrees of self-association and mutual association respectively, c and x being the equilibrium mole fractions of the complexes A_2 and AB. In this case the observed chemical shift is given by the expression:

$$\tau = 2\alpha\,\tau_{A_2} + \beta\,\tau_{AB}, \qquad \text{(II.9)}$$

where τ_{A_2} and τ_{AB} are the chemical shifts of substance A hydrogen-bonded to another species A or B respectively. To facilitate further analysis, the starting point for the reckoning of the chemical shift τ in Eqn. (II.9) was assumed to be the value for substance A in the monomeric state ($\tau_A = 0$). When the degree of self-association is infinitely low ($\alpha \to 0$ for $A_0 \to 0$), we obtain from Eqns. (II.8) and (II.9)

$$(\tau)_{A_0\to 0} = \frac{K_{AB}}{1+K_{AB}}\tau_{AB}, \qquad \text{(II.10)}$$

and the slope of the concentration variation of the chemical shift for the cyclic dimer is

$$\left(\frac{d\tau}{dA}\right)_{A_0\to 0} = \frac{1}{(1+K_{AB})^2}\left[2K_{A_2}\tau_{A_2} - K_{AB}\tau_{AB}\left(1 + \frac{2K_{A_2}}{1+K_{AB}}\right)\right]. \qquad \text{(II.11)}$$

For a linear dimer, the first term in square brackets in Eqn. (II.11) is replaced by $K_{A_2}\tau_{A_2}$.

When monomer-n-mer self-association of one of the components takes place in the solution in addition to association, the asymptotic value of the chemical shift at $A_0 \to 0$ [Eqn. (II.10)] does not change and the limiting slope of the concentration variation of the chemical shift is given by the expression

$$\left(\frac{d\tau}{dA_0}\right)_{A_0\to 0} = -\frac{K_{AB}}{(1+K_{AB})^2}\tau_{AB}. \qquad \text{(II.12)}$$

The presence of an inert solvent in the system alters the conditions defined by Eqn. (II.8). It is then necessary to consider two possibilities.

1. In the general case the concentrations A_0 and B_0 cannot be neglected in comparison with S. Then, bearing in mind that $A_0 + B_0 + S = 1$, we obtain

$$(\tau)_{A_0\to 0} = \frac{K_{AB}P}{1+K_{AB}P}\tau_{AB}, \qquad \text{(II.13)}$$

and the limiting slopes for a cyclic dimer is

$$\left(\frac{d\tau}{dA_0}\right)_{A_0\to 0} = \frac{1}{(1+K_{AB}P)^2}\left[2K_{A_2}\tau_{A_2} + \frac{K_{AB}^2P^2(1+K_{AB})}{1+K_{AB}P}\tau_{AB} - K_{AB}(1+K_{AB}P)\left(1 + \frac{2K_{A_2}}{1+K_{AB}P}\right)\tau_{AB}\right]. \qquad \text{(II.14)}$$

For a linear dimer, the first term in square brackets in Eqn. (II.14) is replaced by $K_{A_2}\tau_{A_2}$. When self-association complexes of an order higher than two (dimers) are present in solution, then

$$\left(\frac{d\tau}{dA_0}\right)_{A_0\to 0} = \frac{K_{AB}P}{(1+K_{AB}P)}\left(K_{AB}P\frac{1+K_{AB}}{(1+K_{AB}P)^2}-1\right)\tau_{AB}\ . \quad \text{(II.15)}$$

Naturally, when $P = 1$, Eqns. (II.13), (II.14), and (II.15) become identical with Eqns. (II.10), (II.11), and (II.12) respectively.

2. The concentrations A_0 and B_0 tend to zero simultaneously ($P \to 0$) so that one can put $S = 1$. Then for dimeric cyclic self-association, we have

$$(\tau)_{A_0\to 0} = 0\ ,$$
$$\left(\frac{d\tau}{dA_0}\right)_{A_0\to 0} = 2K_{A_2}\tau_{A_2} + K_{AB}\tau_{AB}. \quad \text{(II.16)}$$

In the case of linear dimers the first term in the second Eqn. (II.16) is $KA_2\tau A_2$, while in the formation of self-association complexes of an order higher than two (dimers) it is zero.

When several types of equilibria (for example $A + A \rightleftharpoons A_2$, $A + B \rightleftharpoons AB$, and $B + B \rightleftharpoons B_2$ occur simultaneously in solution, simple expressions cannot be obtained for the asymptotic quantities $(\tau)_{A_0} \to 0$, $(d\tau/dA_0)_{A_0}\to 0$, $(\tau)_{B_0}\to 0$, and $(d\tau/dB_0)_{B_0}\to 0$. Several examples of the analysis of such complex systems have been described[111-115].

The chemical shift of the proton in a hydrogen bond can be represented in a general form as a function of the concentrations of the components in solution (x_i), the equilibrium constants for the formation of the association complexes (K_{ij}), and the chemical shifts of the protons in various states (τ_i and τ_{ij}):[12,116]

$$\tau_{obs} = f(x_i, K_{ij}, \tau_i, \tau_{ij}). \quad \text{(II.17)}$$

Eqn. (II.17) can be represented by a power series in terms of x_i, the coefficients of different powers of x_i being mixed non-linear functions of τ_i, τ_{ij}, and K_{ij}. The solution of this system by least squares yields a series of inhomogeneous non-linear equations and therefore the parameters τ_i, τ_{ij}, and K_{ij} are not determined unambigously. More accurate values of these parameters can be found, for example, by the "direct search" method[117].

The procedures described for the determination of the equilibrium constants for different types of association do not take into account the non-ideality of the solution and consequently the values of K are obtained in this way with an accuracy determined by a factor which depends on the activity coefficients of the substances undergoing association[118-120].

The determination of the thermodynamic characteristics of the association process in the presence of simultaneous self-association of the components in solution is a complex problem which becomes considerably simplified when it is known with certainty that one of the components does not undergo self-association and only forms association complexes with the second component.

Then the thermodynamic characteristics of the formation of association complexes may be found from the temperature variation of the chemical shift of the proton in the substance which does not undergo self-association. In the presence of a large excess of the solvent ($B_0 \gg A_0$) the product βA_0 in Eqn. (II.2) may be neglected and the following form of the van't Hoff equation is obtained[84,109,121-123]:

$$R\ln\left(\frac{\tau_A-\tau}{\tau-\tau_{AB}}\cdot\frac{A_0+B_0}{B}\right) = -\frac{\Delta H}{T}+\Delta S. \quad \text{(II.18)}$$

The chemical shift τ_{AB} and the heat (ΔH) and entropy (ΔS) of formation of the association complex are determined from the conditions of the maximum correlation coefficient for the linear equation (II.18) when τ_{AB} is varied.

2. Alcohols

The study of the concentration variation of the chemical shift of the hydroxyl proton in aliphatic alcohols showed[39,40,50] that the degree of their self-association strongly depends on the solvent, being higher in cyclohexane than in carbon tetrachloride and chloroform. This was explained by the formation of intermolecular hydrogen bonds between the alcohol and the solvent, which leads to a decrease of the degree of the alcohol–alcohol self-association. In general, dilution of an alcohol solution by a solvent having basic properties is accompanied by two processes: dissociation of the multimers and association of the monomers with the solvent[39,101,142]. The changes of the chemical shift in the NMR spectra under the influence of these effects are of the opposite sign: the dissociation of the multimers shifts the OH proton signal towards stronger fields, while association with the base causes the opposite shift towards weaker fields. In weakly basic solvents dissociation of multimers predominates and the τ^{OH} signal is displaced towards stronger fields, while in stronger bases association predominates and the τ^{OH} signal is displaced towards weaker fields. Hence it is clear that the shift due to the formation of hydrogen bonds on association will be greater the more acid the solute and the more basic the solvent. This has served as a basis for assessing the relative acidities of many alcohols by comparing their chemical shifts due to the formation of association complexes with the same base[39]. It was shown that the introduction of chlorine atoms into the methyl group of ethanol increases the shift due to the formation of an association complex with the base, i.e. the acidity of the OH proton increases in the sequence ethanol < monochloroethanol < dichloroethanol < trichloroethanol. This sequence is consistent with the increasing inductive effect of chlorine atoms, which is confirmed by the infrared and ultraviolet spectroscopic studies of solutions of these substances[53,125] and also by the pK values[126].

On the other hand, when the alcohol behaves as a base, for example, in a mixture with chloroform, the chemical shift due to association decreases from ethanol to chlorinated ethanol, in agreement with the decreasing basicity of the hydroxyl oxygen in this sequence[51].

Similarly, it has been shown that the capacity of association with a base, and hence the acidity of the OH proton, increases appreciably in the series propanol < prop-1-enol < prop-1-ynol[39], while the opposite sequence holds in chloroform[51].

A comparative study of the formation of association complexes of t-butyl alcohol in acetone and dioxan showed that dioxan is a stronger base[120].

The association of alcohols with various classes of organic compounds has been investigated in a number of studies[30,40,101]. The formation of 1 : 1 association complexes has been observed in the systems benzyl alcohol–acetone[127] and methanol–pyridine[128]. It has been shown[101,129] that alcohols undergo association with nitriles, the strength of the bond in the methanol–acetonitrile association complex being greater than in the methanol–methyl isocyanide complex, in agreement with the results of an investigation

of the vibration spectra of these systems[129]. The bond strength in the association complexes of 2-propanol with *N*-methylacetamide and *NN*-dimethylacetamide[104] is close to that found in the system alcohol–dimethylformamide by infrared spectroscopy[130].

The replacement of the hydroxyl oxygen by sulphur in the alcohol leads to a decrease of bond strength in the association complex with the base[73,131], although the acidity of the proton donor increases. This effect is probably due to the characteristics of the electronic structure of sulphur, which are responsible for the proton-donating and proton-accepting functions of the mercapto-group.

3. Phenols

Phenols, which are stronger acids than alcohols, form more stable association complexes with bases. The formation of such complexes by phenols with various solvents have been investigated in detail by a number of workers.

In the first place one should note the effect of the differences in the acid properties of the phenol and the base on the stability of the complex. Thus the shifts due to the formation of association complexes of 22 phenols with dimethyl sulphoxide are linearly correlated with Hammett's σ constants for substituents, increasing with the acid properties of the phenol[132]. A similar relation was obtained for systems comprising *meta*- and *para*-substituted phenols on the one hand and pyridine on the other[133], which agrees with data for substituted phenol–amine systems obtained by ultraviolet spectroscopy[134,135]. On the other hand, the shift due to association involving phenols is proportional to the basicity of the electron donor[136,137].

A detailed study of systems comprising mixtures of phenols with amines, ethers, sulphoxides, and phosphorus- and carbonyl-containing compounds[138] revealed a linear relation between the shifts due to association and the heats of formation ΔH of the association complexes. Similar results were obtained also by comparing the shifts $\Delta\tau$ due to association and the heats of formation ΔH of the association complexes in phenol–substituted pyridine systems[139]. Earlier similar linear relations were found by comparing the heats of formation of the association complexes with the frequency shifts in the infrared spectra[140,141] and it was emphasised in the second study that a relation of this kind should be observed only for similar compounds with comparable steric effects of the substituents.

With increase of the distance between the atoms forming the hydrogen bond, the strength of the latter diminishes. In agreement with this finding, a linear relation between the chemical shift due to association and the hydrogen bond length was obtained[13] in a study of the association of phenols with bases.

A linear relation between the shift $\Delta\tau$ in NMR spectra and the frequency shift $\Delta\nu$ in infrared spectra on formation of an association complex has been noted in many investigations[13,142-144]. This shows that the variation of these parameters with the electronic structure of the molecules is similar in both cases.

The linear relations examined above, apart from their purely theoretical importance, may also prove useful in determining a number of characteristics of substances which had not been investigated hitherto.

Earlier the effects of intramolecular hydrogen bonds in phenol on its self-association was noted. These bonds have a similar effect also on the capacity of phenols for association. The very weak intramolecular hydrogen bond in *o*-chlorophenol does not prevent either its association even with relatively weak bases such as ether and dioxan[39] or the exchange of the OH proton with methyl alcohol[142]. In contrast, the strong intramolecular hydrogen bonds in *o*-nitrophenyl, salicylaldehyde, and methyl salicylate appreciably hinder their association with basic solvents[39].

Phenols with bulky *ortho*-substituents, which, as already noted, do not undergo self-association in inert solvents, form association complexes with bases, as shown by the shift towards weaker fields of the signal due to the hydroxyl proton in the phenols[28,82-94,150]. The stability of phenol–base association complexes and the chemical shift τ^{OH} on formation of the hydrogen bond diminish with increasing bulk of the *ortho*-substituents in the phenol molecule[28], the association complexes with a stronger base, for example acetone, proving more stable than those with ether.

The study of the association of 2,6-dialkylphenols with dioxan[82] showed that bimolecular complexes are formed in the system. In view of the similarity of the curves relating the chemical shift of the OH proton to the concentration of phenol in dioxan and ethanol, it was suggested[82] that the hydrogen bond in the 2,6-di-t-butylphenol–ethanol complex is formed between the proton of the phenolic hydroxyl and the oxygen of the alcohol. Pokhodenko and Kuts[145], who investigated the effect of the nature of the *para*-substituent in 2,6-di-t-butylphenol on the formation of association complexes with t-butyl alcohol, arrived at a similar conclusion. It was shown that there is a linear relation between the chemical shift of the proton of the phenolic hydroxyl in the association complex and Hammett's σ^- constants for the substituents, with a slope having the same value as in the relation obtained from a similar comparison for monomeric phenols[145-148]. The chemical shift of the hydroxyl proton in t-butyl alcohol on formation of association complexes with phenols also varies linearly with the constants of the substituents in the phenol, but its proportionality coefficient has the opposite sign. This shows that the degree of self-association of the alcohol diminishes with increasing degree of the phenol–alcohol association. These findings are related to the dependence of the stability of the phenol–alcohol association complexes on the electron density at the oxygen and hydrogen atoms in the phenolic hydroxyl. This is consistent with the observed[145] linear relation between the chemical shifts of the proton in the phenol–alcohol association complexes and the association order and also with the autopolarisability of the O...O bond in the complex. Later studies[122] of the temperature variation of the chemical shift of the proton signal from the OH group in a number of *para*-substituted 2,6-di-t-butylphenols on association with ethanol showed that the equilibrium constants and the heats of formation of the association complexes increase linearly with enhancement of the electron-accepting properties of the *para*-substituent in the phenol, i.e. with increase of its acidity. In the same study it was also found that an increase in the stability of the phenol–alcohol association complex entails a lowering of the potential barrier to proton exchange between the phenolic and alcoholic hydroxyls. This finding constitutes experimental confirmation of the opposite variation of the strength of the hydrogen bond (represented by ΔH) and the activation energy E for proton exchange, demonstrated by Sokolov[14,15].

With increased bulk of the *ortho*-substituents in the phenol, the equilibrium constant for the formation of the association complex with methanol diminishes, although the stability of the complex remains virtually unchanged[85]. This is due to the change in the steric effect, as shown by the linear increase of the entropy of formation of the association complex with increasing overall bulk of the *ortho*-substituent. A similar effect of steric factors was observed also in an investigation of the association of 2,6-di-t-butyl-4-methylphenol with aliphatic alcohols[121,123]. It was shown that the heat of formation of the complex changes only slightly on going from methyl to t-butyl alcohol and the change in the degree of association is due to the change in the entropy of formation of the hydrogen bond, which increases linearly with the bulk of the alkyl residue of the alcohol.

The association of phenols with strong bases, such as substituted pyridines, amines, and others is accompanied by the formation of ionic species in which the proton of the phenolic hydroxyl is transferred to the nitrogen atom of the base[39,139,149]. This type of ionisation is more appreciable the more pronounced is the acidic character of the proton donor. The degree of ionisation of course increases on going from alcohols to phenols and from oxygen-containing to nitrogen-containing bases, which are more powerful electron-donating agents.

Complexes of thiophenols with bases have been much less investigated. It is known that their stability is low and as a rule does not exceed 2–3 kcal mole^{-1},[102-103] the degree of association of substituted thiophenols with acetone increasing with the electron-accepting capacity of the substituent due to the increasing strength of the hydrogen bond in the association complexes[151].

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