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Physicochemical and Spectroscopic Characteristics of Associated Compounds and Their Solutions

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In order to make the method of liquid-liquid extraction usable, it is necessary to have the complete characteristics of the liquid systems to be separated. The study and comparison of a range of physicochemical and spectroscopic properties of such systems makes it possible to discover factors affecting the miscibility of the liquids and to establish the presence of specific interactions between the components.

The study of specific interactions with the aim of determining their nature is complicated and requires in each case specific models which include the individual features of the interacting species. When such investigations are combined with the study of solutions by physicochemical techniques, the nature of the solutions and the mechanisms of the processes occurring in them are gradually elucidated.

The present review deals with solubility and the most important physicochemical methods for the investigation of the hydrogen bond in solutions. Certain problems in infrared spectra associated with the effects of general and specific intermolecular interactions and the effect of hydrogen bonds of the type OH...O=C in systems with ketones and aliphatic acids are discussed.

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1. INTRODUCTION

The technique involving the extraction of substances from their solutions by other solvents depends on a knowledge of the miscibilities of the components. A number of publications deal with miscibility in liquid systems. In some of these the results of experimental measurements of miscibilities are reported, while in others the variation of the binodal curve with temperature is discussed or the partition coefficients are quoted. However, experimental data on the effects of hydrogen bonds and of the molecular structures of the components on the miscibility are presented in only a few papers.

Physicochemical methods of analysis provide information about the nature of the processes occurring in these systems. On the other hand molecular spectroscopy is a direct method whereby it is possible to determine the interacting groups and the structure of the compounds formed. Indirect methods frequently fail to yield unambiguous information concerning this problem.

The elucidation of the mechanism of the interaction between the components of liquid systems requires the investigation and the comparison of a range of physicochemical and spectroscopic characteristics of the solutions.

2. SOLUBILITY AND CERTAIN PHYSICOCHEMICAL PROPERTIES

Solubility constitutes one of the most distinctive effects of intermolecular forces. Mendeleev believes that solutions are the best subjects for the investigation of the general phenomena of chemical interactions. He regarded dissolution as a chemical process leading to the formation of definite and indefinite compounds without a sharp boundary between them and the solutions as "liquid dissociation systems consisting of species of the solvent, the solute, and definite unstable but exothermic compounds formed by them, one or several, depending on the nature of the constituent elements"[1].

In solutions there is a very wide variety of chemical interactions leading to the formation of compounds of different stabilities and therefore solutions may play a significant role in the solution of the general problem of the nature of a chemical compound. Mendeleev wrote that "in the solution there must be association between species of different kinds, interacting chemically, combining, breaking down, or forming systems". This involves the operation of forces of different intensities which lead to the formation of compounds of different stabilities. According to Mendeleev[2], "it is futile to seek simplicities ranging over the entire scale of dissolution [phenomena]. It is futile to seek a function expressing the sum total of the observations". And further[3]: "...the formation of solutions may be regarded from two aspects: physical and chemical and in solutions it is more evident than elsewhere how close to one another are these two aspects of natural science". Mendeleev in fact chose solutions for the investigation of the problem of chemical compounds.

The aim of the modern studies on the problem of solubility is to establish special relations governing the dissolution of individual groups of substances in solvents of the same chemical type. Up to the present time, there has been no quantitative theoretical calculation of the solubility in the majority of cases. Theoretical advances are restricted mainly to the derivation of qualitative and semiquantitative relations. On the other hand, the creation of a quantitative theory of solubility would extend greatly the possibilities for the discovery of laws governing the intermolecular forces in concentrated solutions and for the investigation of the internal structure of solutions.

Attempts to set up a theory of solubility and to establish a physical and chemical standpoint concerning solutions were undertaken by Shreder[4], Semenchenko[7-9], who interpreted the solubility data in Seidel's handbook[10], and Shakhparonov[11-14].

The complex problem of intermolecular interactions has been solved only for rarefied gases, i.e. for the case where the intermolecular distances greatly exceed molecular dimensions. On the other hand, in the study of the

liquid state we encounter distances close to equilibrium and the familiar expressions for orientation, polarisation, and dispersion forces cease to be valid; this makes it difficult to give a satisfactory description of intermolecular interactions in the liquid phase.

Furthermore, the liquid state of matter is characterised by a wide variety of types of interactions between the molecules. These include both different types of classical van der Waals interactions (orientation, inductive, and dispersion interactions) and physicochemical interactions of a wide variety of types (complex formation and hydrogen bonding).

Interactions of the first type (general intermolecular interactions) result, after averaging with respect to configuration and volume, in the effect of the solvent as a physical dielectric medium (volume dielectric effect).

Interactions of the second type, a characteristic feature of which is that they are directional, are physicochemical in nature and in fact lead to the formation of a fairly strong bond between molecules, the energy of which is nevertheless significantly lower than the energy of the chemical bond. Evidently this type of interaction is determined to a greater degree than the first by the individual properties and the nature of the solute and solvent molecules (specific intermolecular interactions).

The types of interaction discussed above are not of equal importance. Systems may exist in which specific interactions of one type or another are absent while van der Waals interactions are observed in all cases. The study of the specific interactions with the aim of elucidating their nature is undoubtedly very complex and requires definite models for each case which take into account the individual features of the interacting species.

The physical and chemical properties of water, alcohols, acids, proteins, and many other practically important substances depend significantly on the interaction of two functional groups of one or different molecules.

The formation of hydrogen bonds is a principal factor which determines the nature of the changes in the majority of physical and certain chemical properties in solution or in the pure substance. This is quite reasonable, since the formation of a hydrogen bond can alter not only the mass, dimensions, and the shape of the species and the distribution of individual atoms but also the electronic structures of the functional groups.

Hydrogen bonds were discovered for the first time by Il'inskii[15] in a study of solubility and were then found also by other classical methods in the study of vapour pressure and density, molecular weight, dielectric constant, distribution between different phases, molar volume, refractive index, electrical conductivity, and thermal conductivity.

Depending on molecular structure, intermolecular hydrogen bonds can lead to different types of association, complexes, structures with a multiplicity of bonds, chains, rings, and three-dimensional networks.

The differences in the types of association complexes formed via hydrogen bonding is one of the principal causes of the differences between the physicochemical properties of these substances in the liquid and solid states. As emphasised by Hildebrand[5], not all deviations should be attributed to one factor only. At the same time there is no doubt that in many cases a significant proportion of the deviations in the physicochemical properties of liquids and solutions are in fact determined by hydrogen bonds.

The capacity of various classes of organic compounds for the formation of hydrogen bonds was thoroughly investigated by Ewell et al.[16], who developed a simple classification, according to which different liquids were divided into five groups.

One must emphasise not only the quantitative but also the qualitative differences between three-dimensional association complexes (networks) and cyclic dimers and also between chain association complexes and cyclic dimers. Therefore Ewell is not quite correct in combining into a single class alcohols, acids, and amines. Acids, which form almost exclusively cyclic dimers, should constitute an entirely separate class. The system proposed provides a basis for qualitative predictions when only the dissociation or formation of hydrogen bonds takes place. In those cases where dissolution disturbs an existing equilibrium or sets up a new one, the classification is of less value.

The different amounts of molecules combined into association complexes and their continuous time variation make it difficult to apply the familiar thermodynamic postulates in the calculation of the dynamic equilibrium between such complexes. There is a complicated relation between the strength of a hydrogen bond of a given type, the average "lifetime" of association complexes with different numbers of molecules, and the capacity of molecules of different structures to form several hydrogen bonds simultaneously. All these problems become even more complicated when solvates are formed from different component molecules.

As pointed out by Landsberg[17], Malyshev[18], and Batuev[19-21], the solubility of water, methanol, and formic acid in acetone and dioxan is due to the dissociation of the hydrogen bonds of the pure substance and the formation of new bonds between solvent and solute molecules.

It has been established[22] that, in addition to hydrogen bonds of the type OH...O and N−H...O observed in water, alcohols, phenols, carboxylic acids, and ammonia, hydrogen bonds of the type C−H...O or C−H...N are formed on dissolution of chloroform, bromoform, or hydrogen chloride in solvents containing oxygen and nitrogen. This was confirmed by measurements of the viscosities[23], dielectric constants[24], and freezing points of these solutions[25].

The most important methods for the investigation of hydrogen bonds in solutions, are, apart from spectroscopic procedures, those based on the determination of dielectric properties of the liquids, the measurement of the vapour pressure, cryoscopy, and the study of solubility, partition between phases, viscosity, and density.

The theory of the dielectric constant may be regarded as a supplement to the modern theory of the liquid state. Dielectric properties arise as a statistical average result of many microprocesses. Hypotheses concerning the relation between dielectric properties and structure have been put forward by Girard[26]. He believes that monohydric alcohols can form two types of association complexes—polar and non-polar, the former predominating in primary and secondary alcohols and the latter in tertiary alcohols by virtue of the characteristics of their structure. Accordingly in the first case there is an anomalous increase in polarisation and in the second a decrease. The temperature variation of polarisation confirms that the breakdown of association complexes of the first type should make the decrease of the dielectric constant with temperature more rapid and the breakdown of association complexes of the second type should not only reduce the temperature-induced decrease of polarisation predicted by theory but should in fact result in an increase of the dielectric constant. This has been confirmed experimentally for certain isomers of higher alcohols[27] and also pyridine[28] and carboxylic acids[29,30]. The dielectric properties of acetic,

propionic, butyric, and valeric acids are characterised by an increase of the dielectric constant with temperature[30-35]. The dielectric constants of caproic, oenanthic, and caprylic acids are almost invariant in the temperature range investigated[36]. These phenomena are usually explained by the formation of non-polar dimers in the liquid state.

The views on the mechanism of the effect of temperature on the dielectric constant are extremely varied. The most reasonable is the hypothesis that the formation of hydrogen bonds in the dimer may entail a significant change in the dipole moment of the molecule not only as a result of dipoles induced by long- and short-range forces but also in consequence of the super-position under these conditions of the electron clouds and the redistribution of electron density in the dimer. With increase of temperature, the hydrogen bonds in the dimer are deformed and their length changes, which leads to a change in the vibration frequencies of the molecule and the paramagnetic resonance signals[37-39]. Kerr's molecular constants calculated from measurements of the dielectric constants of dilute acetic acid solutions in benzene suggested[40] that a centrosymmetric planar conformation is most likely for carboxylic acid dimers. On the other hand, calculation of the same quantities for the dioxan–acetic acid complex showed that the latter has a non-planar structure and the angle φ between the molecular planes of the acid and dioxan is approximately 80°. Thus in the general case the effect of the hydrogen bond on the dielectric properties must be considered in two ways—as a factor responsible for the correlation between the relative orientations of molecules and as a factor leading to an additional change in the molecular dipole moment.

The cryoscopic method has been widely used for studies on the hydrogen bond, mainly for a qualitative assessment of the possible existence and type of association complexes and also for the determination of the equilibrium constant K_n in the association processes investigated. Cherkashin[41,42] determined cryoscopically the degree of association and the molecular composition of a number of organic substances dissolved in benzene, in particular[43,44] propionic and acetic acids. The average association constants K_n for acetic and propionic acids proved to be 0.5×10^5 and 1.5×10^3 respectively. According to Cherkashin's data, the straight line for the ideal dimer ($K_n = \infty$) and the calculated curve for acetic and propionic acids differ very appreciably from the experimental curves, which the author explains by an intermolecular field interaction and a weak chemical interaction with formation of readily dissociable association complexes. The author confirmed that acetic acid in benzene solution has the molecular composition $(CH_3COOH)_2$. The marked deviation from the ideal dimer curve in the case of formic acid is explained by chain association and a sharp change in the composition of the molecules as a function of the concentration of the acid.

Lutskii's studies[45,46] showed that density and viscosity data for solutions may be used to establish qualitatively the presence and nature of the association of the solute. The author showed that, when alcohol and benzene are used as solvents, the variation of the density and viscosity is the same despite the postulated difference in the nature of association in these different solvents, the variation being the same not only qualitatively but also quantitatively. The author explains this by postulating that in the comparatively concentrated solutions investigated, the species involved in association with the molecules of the solvent (alcohol, benzene) are not single molecules of the test substance but groups. The latter evidently do not break down on dissociation. It is interesting that the relations found for the densities and viscosities of aromatic acids in benzene and alcohol are similar to those observed for the pure substances in the liquid state; the author believes this makes it possible to draw inferences concerning the presence and nature of association of the solute based on the densities of the solutions.

The properties of aqueous acid solutions have been investigated by a number of workers. The viscosities, densities, and critical temperatures of the systems acetic acid–water and butyric acid–water have been studied by Solomko[47]. The viscosity and density isotherms for these systems have maxima, occurring at the same composition in the acetic acid–water system. For the system butyric acid–water, the density maximum is displaced towards higher water contents.

Golik et al.[48] investigated the kinematic viscosities of acetic and butyric acids in water at 30–90°C and established that the viscosity isotherms of aqueous acid solutions have maxima, which are more pronounced the higher the critical point of the acid and the greater the difference between the viscosities of the components. With increase of temperature, the maximum is somewhat reduced. The complex concentration variation of the viscosity is explained by the formation of structural entities due to the interaction between the carboxy-groups of the acids and the hydroxy-groups of water. Glagoleva studied the equilibrium in the system formic acid–water[49] and the viscosities and specific gravities[50,51] of the systems formic acid–water and acetic acid–water. These data established the formation of the compounds $HCOOH.H_2O$, $HCOOH.2H_2O$, $CH_3COOH.H_2O$, and $CH_3COOH.2H_2O$. In a study of the heats and integral heats of dilution of formic acid solutions, Glagoleva[52] established that these quantities are a maximum when the solution contains 1–2 moles of water per mole of acid. She assumes that, for aqueous solutions containing two moles of water for each two moles of acetic acid, a hydrate with a chain structure and a dimer with the composition $2CH_3COOH.2H_2O$ are formed, while in the presence of two moles of water per mole of acid the species produced is a hydrate with the composition $CH_3COOH.2H_2O$. These hypotheses were subsequently confirmed by Glagoleva herself[53] and other investigators[54-57] using Raman spectroscopy.

Spectroscopic investigations are particularly important in the study of the structure of liquids and solutions. The study of the molecular spectra of solutions reveals more clearly the role of individual groups of atoms in the molecule in the formation of intermolecular bonds.

3. INFRARED SPECTROSCOPIC EFFECTS OF UNIVERSAL AND SPECIFIC INTERMOLECULAR INTERACTIONS

Real systems can be adequately described only by taking into account the collective and individual effects of the molecules in the surrounding medium on the spectrum of the molecule in solution. However, at the present time there is no rigorous and logical theory of the effect of intermolecular interactions on the infrared spectra of solute molecules. Therefore the subdivision of interactions into general (collective) and specific (individual), which entails the introduction of model hypotheses in the study of specific interactions taking into account the individual features of the interacting species, is justified although it is in fact extremely arbitrary, and in real systems there is a continuous gradation from pair interactions to the overall effect of the surrounding species on the solute molecule[58].

The conditions under which the test molecule in solution interacts with a light wave differ from those for an isolated molecule. This is the reason why it is necessary to introduce generalised parameters such as the dielectric constant and the refractive index, which take into account the effect on the test molecule of the sum total of the surrounding species treated as a physical medium. The concept of a reactive field, introduced by Onsager [60], acting on the molecule from the direction of the adjacent species surrounding it, which it has polarised, proved to be extremely fruitful in this respect. Kirkwood [61] and Bauer and Magat [62] showed on the basis of the Onsager model that, when the infrared vibration is regarded as that of a simple oscillating dipole, then its frequencies in the vapour phase (ν_V) and in solution (ν_S) are related by the expression $(\nu_V - \nu_S)/\nu_V = C(\epsilon - 1)/(2\epsilon + 1)$. In this relation ϵ is the dielectric constant of the solvent and C is a constant. It holds best for solvents of low polarity in which the interaction between the solute and solvent molecules is slight. These theories are difficult to test quantitatively because of the impossibility of determining the coefficient C, which depends on assumptions about the dimensions and form of the overall orientation of solvent molecules around the solute molecules and cannot be found experimentally.

Plots of $(\epsilon - 1)/(2\epsilon + 1)$ against $(\nu_V - \nu_S)/\nu_V$ are straight lines for non-polar solvents, while for solvents with proton-donor or proton-acceptor properties the points deviate appreciably from linearity. Probably in those cases the effect of polarisation interactions which occur in non-polar solvents is supplemented by an effect due to the orientation of the solvent molecules or an effect caused by the formation of a molecular complex [63]. A dielectric theory of the effect of the solvent on the infrared spectra of molecules has been developed by Pullin [64,65]. He suggested that the frequency shift depends in the general case both on the dielectric constant ϵ and the refractive index n_0 of the solvent as well as on the molar volumes V of the solvent and the solute which is included implicitly in the expression for the radius of the Onsager cavity. Pullin proposed the following function $f(x,V) = (1/V)(x - 1)/(2x + 1)$, where $x = \epsilon$ or n_0^2 and V is a characteristic of the dimensions of the Onsager cavity. Buckingham [66,67] explained the effect of the solvent on the infrared spectra of molecules from the standpoint of both general and specific interactions. Bellamy and coworkers [68,69] showed that the problem of the effect of the solvent on the infrared frequencies of solid molecules cannot be solved taking into account the general effect only. Not only dielectric effects but also specific interactions, expressed in the formation of association complexes of the solute and solvent molecules, play a dominant role, while the association complexes may have various natures. Thus, when polar media (alcohol, water) are used, association complexes are formed as a result of hydrogen bonding and, according to Bellamy's postulates [70], the higher the polarity of the bond the greater the relative frequency shift.

Thus the possibility of treating the effect of the solvent on the intensities and positions of the infrared bands is very limited. In the general case specific interactions are always observed against the background of the general effect of the medium.

The spectroscopic method for the investigation of molecular association due to hydrogen bonding is fundamental; it is the only procedure which makes it possible to elucidate the distribution of atoms in the vicinity of donor and acceptor groups and the mechanism of the formation of the hydrogen bond.

The forces responsible for the formation of the hydrogen bond differ in magnitude from those which give rise to the ordinary chemical bond. In the general case the energy of the hydrogen bond consists of the electrostatic energy E_{el}, donor–acceptor interaction (with participation of the s orbital of the hydrogen atom) and π-electron interaction arising by virtue of the participation of the π orbital E_π of the hydrogen atom [71]. The role of the individual components in different types of hydrogen bonds may not be the same.

The spectra of compounds forming hydrogen bonds have been investigated in particular detail by Landsberg and coworkers [72-74], Chulanovskii and coworkers [75-80], Batuev [19-21], Stepanov [81-83], Vol'kenshtein [84], and Sokolov [85-87]. They developed a theory of hydrogen bonds on the basis of experimental studies of the spectroscopic effects of hydrogen bonds in many of the most important substances (alcohols, organic acids, etc.). The causes of the formation of the hydrogen bond were examined systematically by Sokolov [88,89]. The conditions necessary for its formation reduce to the asymmetry of the interacting groups. In order to elucidate finally the distribution of electron density in the hydrogen bridge, experimental data must be resorted to. Infrared spectra do not provide information about changes in electron density near the hydrogen atom. On the other hand, proton magnetic resonance spectra, where the displacement of the signal is very sensitive to the formation of a hydrogen bond, are more suitable for this purpose. According to Aleksandrov and Sokolov [90], the change in the screening of the proton on formation of the complex RA–H...BR′ probably depends (1) on the change in the polarity of the A–H bond (a shift of the centre of gravity of the electron cloud of this bond towards the atom A), (2) on the extension of the A–H bond, (3) on the formation of the donor–acceptor bond H...B, which leads to a shift of the centre of gravity of the cloud of the unshared pair of electrons of B towards the atom H, (4) on the effect of the electric field of the dipole of the BR′ molecule, and (5) on the effect of the unshared pair of p electrons of the atom B (or the B–R′ π bond). The increase in the proton magnetic screening constant σ due to the increase of polarity on formation of the donor–acceptor H...B bond probably plays a dominant role. Thus Sokolov [85-87,91] concentrates attention on the change in the infrared absorption spectrum of the ν_S stretching vibrations and on proton transfer processes.

When a substance dissolves, various absorption bands may show perturbation of different magnitudes and types. Two types of such perturbation have been established [76,77]—bulk-phase and local. In the bulk-phase interaction the state of the molecule is determined by a large number of surrounding molecules, and in a gradual change of the composition of the solvent the characteristics of the absorption band also gradually alter.

Local interactions are extremely varied and are of different types even in the case of a thoroughly investigated type of intermolecular interaction such as hydrogen bonding. The state of the active group of the absorbing molecule is determined by several adjacent molecules and the changes in the spectroscopic characteristics of the bands are discrete. The effect of the local intermolecular field on the infrared absorption frequency associated with the C=O stretching vibrations in ketones has been investigated by Gadzhiev [92] over a wide range of temperatures (from +80° to −180°C). The observed shifts of the C=O stretching vibration bands of ketones on lowering the temperature are accounted for by an increase in intermolecular interaction due to a decrease of the distance between the mole-

cules and an increase in the residence time of the molecule in the state of equilibrium. The temperature variation of the shift in the infrared absorption band of the C=O group of ketones is linear.

On transition from one type of local bond to another, i.e. on breakdown of one and formation of another association complex, observed on dissolution, the following changes may occur in the vibration spectrum: (1) the stretching-vibration bands are displaced towards lower frequencies (compared with the absorption band for an isolated molecule) and the position of the maximum of the band depends on temperature—the lower the temperature the greater is the displacement of the maximum towards lower frequencies; however, exceptions are also known [77,93], when the formation of local bonds does not cause a bathochromic shift of the stretching vibration bands; (2) there is an appreciable change in absorption intensity, which is sometimes very large for the fundamental bands of the stretching vibrations involved in the formation of the molecular bond; here the discrete structure is more complex than in cases where a shift does occur; (3) the absorption band due to these bonds becomes appreciably broader.

When association complexes break down in a pure liquid or in a solution, converse changes occur in the characteristics of the stretching vibration band. The most typical difference between the molecular bonds of the newly formed association complexes on the one hand and the chemical bond in molecules on the other consists in the ready reversibility of the association process under normal conditions due to the thermal motion of molecules, a wide variety of possible interactions between molecules, and an insufficiently defined nature of the association complexes produced.

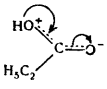
All these factors complicate our understanding of the molecular state in solutions. Furthermore, in contrast to the solid state, in liquids there is a possibility of the coexistence, with different probabilities, of various types of intermolecular hydrogen bonds, including those which do not correspond to the absolute potential energy minimum [78].

Structural changes in solutions can be investigated in greater detail by spectroscopic procedures than by physicochemical methods. In the structural analysis of the solutions the elucidation of the structural elements of molecules responsible for the intermolecular bond and its type and also the nature and strength of intermolecular association are of interest.

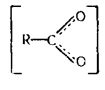
4. SPECTROSCOPIC EFFECTS OF HYDROGEN BONDS OF THE TYPE OH...O=C

Spectroscopic effects of hydrogen bonds of the type OH...O=C have been usually investigated on the basis of data for the O–H stretching vibrations, which made it possible to assess the state of the hydrogen atom alone [94]. A more detailed study of this bond indicates the necessity of elucidating the role of at least three atoms (A, H, and B) in the schematic structure of the hydrogen bond RA–H...BR′. For this, it is necessary to investigate not only the A–H spectrum but also the spectra of the R–A and B–R′ groups. On the other hand, the formation of the bond OH...O=C entails a change in the stretching vibration frequencies of both O–H and C=O groups. Although the shift is in this case smaller, the overlapping by other bands (C–H, O–H) is also less pronounced in the study of equilibria involving associated substances such as, for example, water and alcohols.

According to infrared spectroscopic data, the carboxy-groups of aliphatic acids have an asymmetric structure: the proton is located within the electron cloud of one of the oxygen atoms [95]. The properties of acids and quantum-chemical considerations [96] make it possible to attribute the following formula to propionic acid for example:



The frequency of the carbonyl group is very sensitive to interaction with other bonds [97]. Depending on the nature of the substituent in the organic group, the position of carbonyl bands can be somewhat displaced [98–100]. When an aliphatic group is replaced by an aromatic group, the band is displaced towards longer wavelengths (1690 cm^{-1} in the spectrum of benzoic acid). The presence of electrophilic substituents in the organic group gives rise to a hypsochromic shift: 1735 cm^{-1} in the spectrum of monochloroacetic acid [98] and 1730 cm^{-1} in that of α-chloropropionic acid [101]. This phenomenon can be explained directly by the mutual effects of the bonds: the partial shift of the electron to the C=O bond or, conversely, a shift of the C=O electron to an electron-acceptor group. When an electron is transferred to the C=O bond, the force constant of the latter k_{C-O} and hence the frequency are reduced, while in the opposite case they are increased. On the other hand, spectra of the ions derived from the acids do not contain such frequencies but they do include characteristic bands in the region 1510–1650 cm^{-1} (antisymmetric vibration of the COO^- group) and at about 1400 cm^{-1}, corresponding to the symmetrical vibrations of this group [96,102,103]. The spectrum changes in this way because both oxygen atoms in the ion, linked to a carbon atom, become equivalent:



The carboxylate ion has a symmetrical structure in aqueous solutions of acid, where it is formed as a result of acid dissociation, and also in salts where the metal atom is equally associated with both oxygen atoms [96]. It must be noted that the stretching-vibration frequency of the carbonyl group at about 1700 cm^{-1} is due to C=O groups hydrogen bonded into dimers and is most intense in the infrared. However, this band may not always be observed or can be observed very weakly in the Raman spectrum. If the dimer formed by the association of acids has a centre of symmetry, only antisymmetric vibrations will be active in the infrared spectrum, while in the Raman spectrum symmetrical vibrations will be active [104], where the corresponding carbonyl frequency is 1660 cm^{-1}. The appearance of a frequency in the range 1660–1670 cm^{-1} in the infrared spectrum is associated with the breakdown of ring symmetry in the liquid phase as a result of the interaction between the dimers.

In a number of studies the effect of hydrogen bonding and association of liquid acids on the frequency and intensity of the C=O characteristic vibrations was considered [55–57,104–106]. Gillette and Daniels [106] observed a change in the structure of the C=O band over a wide temperature range in the vapour phase. The authors interpreted the structural changes of the bands as due to the simultaneous presence of monomeric and dimeric acetic acid species.

Batuev [55–57] compared the Raman spectra of liquid formic, acetic, isobutyric, and isovaleric acids at room temperature and concluded that the carbonyl group is

extremely sensitive to the formation of a hydrogen bond and under its influence the C=O frequency undergoes a considerable shift, spreading into broad diffuse bands. Depending on the number and positions of the C=O absorption bands, Batuev divided acids into three groups: formic acid with frequencies at 1670 and 1724 cm^{-1}, acetic acid with frequencies of 1665, 1713, and 1740 cm^{-1}, and the remaining acids characterised by a single frequency in the form of a narrow line in the range 1660–1670 cm^{-1}. He believes that association in formic and acetic acids is largely of a polymeric type, in contrast to heavier acids, which may be regarded as dimeric. However, Smolianskii[107] observed in the infrared spectrum of liquid isobutyric acid a second component (on the high-frequency side) of absorption band due to the hydrogen-bonded C=O group. The doublet structure of the band is explained by the presence of open-chain dimers in the acid, which is confirmed by an increase in the intensity of the high-frequency component at 1720 cm^{-1} as temperature is increased.

Feneant-Emard[108] confirmed Batuev's observation in the study of the Raman spectra of acids and at the same time discovered a higher frequency, at 1760 instead of 1740 cm^{-1}. He noted that both these bands can probably be attributed to an open-chain dimer, since the adoption of the hypothesis of polymeric chain association would probably entail a very low concentration of non-hydrogen-bonded groups at the end of the chain, which could not be detected in the Raman spectrum.

Constant[109] showed by ultrasonic spectroscopy that not only acetic acid polymers but also polymers of aliphatic acids with longer chains exist. He believes that the percentage polymerisation increases with the length of the carbon chain of the acid.

Lascombe et al.[110] found from the position of the C=O band in the infrared spectra of liquid propionic, butyric, and caproic acids that the carbonyl group gives rise to a band at a lower frequency than for the free C=O group in inert solvents, in addition to the band associated with the dimer. The relative intensity of the second component in the spectra of these acids is reduced with increasing carbon chain length. These workers believe that the appearance in the infrared spectrum of the band at 1748–1755 cm^{-1}, like that of the band at 1740–1760 cm^{-1} in the Raman spectrum, is associated with the formation of polymers in which only the OH component of the carboxy-group is involved in hydrogen bonding, in agreement with Constant's data[109]. On the other hand, the intensity of the high-frequency component of the dimeric band is directly related, as noted by Feneant-Emard, to the molecular weight of the polymer. However, Lascombe et al. believe that the presence of this band cannot be accounted for solely by the existence of open-chain dimers because in this region there is also a band which is observed in the spectra of solutions when the solvent is a proton acceptor

and the structure $R-C(=O)\cdots OH\cdots Y$ is attributed to the complex formed.

Shubin[111,112] investigated the hydroxyl band in the infrared spectra of formic, acetic, propionic, butyric, isobutyric, and isovaleric acids in the gas and liquid phases. He showed that the position and shape of the absorption bands, which characterise the bond involving the hydroxy-group and also the extinction coefficient, scarcely change on transition from the gas to the liquid phase. Formic acid was an exception. For formic acid, the band in the spectrum of the liquid phase is somewhat broader than for the gas phase, which can be accounted for by the partial chain association of the acid in the liquid phase. This suggested that the type of association of the acid in the liquid phase is the same as in the gas phase, for which dimeric association has been established by Pauling and Brockway using electron diffraction[113]. The temperature variation of the absorption maximum in the band due to the dimer makes it possible to determine the heats of dissociation of formic, acetic, propionic, butyric, isobutyric, and isovaleric acids in the gas phase. The energy of the OH...O=C bond proved to be the same for all the acids investigated (except formic) and approximately equal to 8.3 kcal $mole^{-1}$.

The relations governing the effect of adjacent atoms on the intensity and frequency of the stretching vibrations of the carbonyl group in carboxylic acids are similar to the relations characteristic of ketones. Since there have been only a few infrared spectroscopic studies of the carbonyl group in monocarboxylic acids using solvents of different types, we shall employ studies on the carbonyl group of ketones in the comparison.

Bottreau et al.[114] studied the effect of non-polar solvents (hexane) on the stretching vibration frequency of the carbonyl group of ketones. A detailed study led to the conclusion that the observed spectroscopic changes are a result of two simultaneous effects.

1. *Effect of the breakdown of ketone association complexes.* When two associated adjacent molecules $\left(\overset{+}{C}=\overset{-}{O}\right)$ $\left(\overset{-}{O}=\overset{+}{C}\right)$, each of which is in the electric field of the other are considered, the direction of the field displaces the electrons of the double bonds towards the oxygen atom. Dissolution in hexane leads to the separation of the dipoles and enables the displaced electrons to return to the C=O bond; this is accompanied by a progressive increase in the carbonyl vibration frequency.

2. *The Kirkwood effect.* Dissolution of ketones in the test solvent (carbon tetrachloride, hexane, cyclohexane) decreases the dielectric constant of the medium (reflected in an increase of the vibration frequency of the carbonyl group). Wishing to elucidate the contributions of the two effects, the authors eliminated the effect due to bond dissociation by hydrogen bonding the ketone molecule to phenol molecules before dilution with the solvent. This made it possible to observe the influence of the Kirkwood effect on the carbonyl frequency alone. It is easily seen that, whereas inert solvents increase the carbonyl frequency in ketones, in proton-donor solvents such as chloroform, bromoform, and butanol the C=O frequency falls as a result of the formation of a complex of the type C=O...H–C or C=O...H–O. Thus the C=O stretching vibration frequency is 1715 cm^{-1} in pure acetone, 1722 in hexane solution, 1721 in cyclohexane, 1717.5 in carbon tetrachloride, 1709.5 in chloroform, 1707 in bromoform, and 1709 in butanol. The carbonyl group in carboxylic acid monomers behave similarly.

The change in the antisymmetric C=O frequency of the acid dimer and of the C=O frequency of the monomer is different in solvents of different types. The C=O stretching vibrational band due to the acid dimers depends on the polarisability of the solvent. In solutions with a high concentration of the acid, polarisation diminishes due to the dimerisation of the acid molecules. Conversely polarisation increases in inert solvents (heptane, carbon tetrachloride) on dilution. This is caused by the presence in certain such solvents of a mixture of highly polar single

acid molecules and weakly polar or non-polar dimers. These changes in the polarisation of the solution have an effect on the C=O vibration frequencies of the acid dimers, altering the ring symmetry and the frequency of the dimer carbonyl group. Solutions of acids in solvents capable of forming hydrogen-bonded complexes have been investigated to a much lesser extent and the interpretation of the results is much more complicated.

In Denisov's systematic studies [115,116] problems of the effect of the hydrogen bond of the type O–H...O=C on the stretching-vibration band of the carbonyl group in ketones were considered. Denisov showed that in liquid systems containing a strong acid (acetic, mono-, di-, and trichloroacetic, trifluoroacetic) and a ketone the formation of a mixed complex predominates over the dimerisation of acids. The absorption spectra of cyclohexanone (0.39 M) and trichloroacetic acid (0.016 M) in carbon tetrachloride contain bands due to cyclohexanone (1717 cm^{-1}), acid dimers (1751 cm^{-1}), and acid monomers (1787 cm^{-1}). On the other hand, these bands are absent from the spectrum of a mixture of cyclohexanone and trichloroacetic acid and are replaced by bands corresponding to interaction products.

Denisov assigned the 1764 cm^{-1} band to the carbonyl vibrations of the acid, the hydroxy-group of which is involved in hydrogen bonding with the ketone. The 1691 cm^{-1} band is interpreted as due to the C=O frequency of the ketone participating in hydrogen bonding with acid molecules. By investigating the dependence of the parameters of the C=O band on the properties of the components of the complex, the author showed that the spectroscopic characteristics of the C=O band of the ketone involved in hydrogen bonds of the type C=O...HO depend not only on the properties of the C=O group but also on those of the OH group. The same may be said of systems containing a strong acid and an ether [117], nitrile, ester, or another molecule with sufficiently strong electron-donating capacity.

The formation of an acid–ketone complex was observed also by Reeves [118] in a study of hydrogen bonding by proton resonance. He showed that, in a solvent with pronounced electron-donor properties such as acetone and acetonitrile, dimeric acid molecules are involved in the equilibrium between the hydrogen-bonded complex and the monomer of the type

$$[RCOOH]_2 + 2D \rightleftarrows 2RCOOH \cdot D,$$

where D is a powerful electron donor.

We may note that in the spectra of solutions of acids in solvents which are powerful proton acceptors (ethers, esters, ketones, acetonitrile, dioxan) one band is always observed [98] in the region of the stretching vibrations of the carbonyl group. Only at a concentration equal to or exceeding 10^{-1} M does a band characteristic of the dimer appear at low frequencies. One may predict that, by analogy with the behaviour of ketones in proton-donor solvents, complexes of the type C=O...H–O will form with acids, as a result of which the intensity of the acid monomer band increases relative to the dimer band and is somewhat displaced towards lower frequencies. It becomes clear that even more complex interactions will be observed in solutions where the solvent behaves both as a proton donor and acceptor.

Water molecules possess both proton-donor and proton-acceptor properties. Both these properties in water as a solvent are weak, because the majority of the hydrogen and oxygen atoms are involved in the formation of the intermolecular hydrogen bonds of water itself. The solubility of carboxylic acids in water has been investigated because of their importance in biology and chemistry. However, few acids other than formic and acetic have been investigated (spectroscopically) and only over a narrow range of concentrations. Table 1 presents spectroscopic data for two-component monocarboxylic acid–hydroxylated solvent systems. The Table shows that a band due to the C=O group in acids is sensitive to association and the formation of a hydrogen bond. Furthermore, in the study of the carbonyl stretching vibration band it appears possible to obtain data concerning the immediate environment of the COOH group, which is particularly important in the investigation of the properties of solutions in the acid extraction process. We shall consider some of these studies.

Table 1. Raman frequencies of two-component systems monocarboxylic acid–hydroxylated solvent.

Solvent	Acid	Concn. of acid	Frequency, cm^{-1}	References
H_2O	HCOOH	10–15%	1660 w., 1710	19–21, 55–57
H_2O	HCOOH	40%	1708	119
H_2O	HCOOH	1:2	1712	120
H_2O	CH_3COOH	10%	1710	19–21 55–57
H_2O	CH_3COOH	dilute aqueous soln.	1710	120[a]
H_2O	CH_3COOH	conc. soln. with a small amount of water	1730, 1660, 1766 w..	120
H_2O	CH_3COOH	10 mole %	1710	121
CH_3OH	CH_3COOH	10 mole %	1707	121
C_2H_5OH	CH_3COOH	10 mole %	1707	121
C_4H_9OH	CH_3COOH	20–40 mole %	1706, 1736	121
C_4H_9OH	CH_3COOH	60–80–90 mole %	1660, 1703, 1745	121
H_2O	CH_3COOH	83.5 wt.%	1697, 1665, 1745	122
H_2O	CH_3COOH	78.8 wt.%	1690, 1667, 1745	122
H_2O	CH_3COOH	76.9 wt.%	1700, 1687	122
H_2O	CH_3COOH	65.1 wt.%	1700, 1680, 1760	122
H_2O	CH_3COOH	21.9 wt.%	1700, 1695	122
H_2O	CH_3COOH	1.3 wt.%	1695, 1705	122
H_2O	CH_3COOH	87 %	1715, 1670 w.	91[b]
H_2O	CH_3COOH	equimolar soln.	1715, 1670 w.	91
H_2O	CH_3COOH	63 %	1715, 1760 w.	91
C_4H_9OH	CH_3COOH	10^{-2} M	1710, 1754[c]	110
C_4H_9OH	CH_3COOH	1.0 M	1710, 1754[c]	110
H_2O	C_2H_5COOH	equimolar soln.	1720, 1708, w., 1750 w.[c]	123
C_4H_9OH	C_2H_5COOH	10^{-2} M	1715, 1740[c]	110
C_4H_9OH	C_2H_5COOH	1 M	1715, 1740[c]	110
C_4H_9OH	C_3H_7COOH	10^{-2} M	1709, 1737[c]	110
C_4H_9OH	C_6H_5COOH	10^{-2} M	1708, 1737[c]	110

[a] Frequencies of 1660, 1712, and 1745 cm^{-1} were observed in the spectrum of pure acetic acid.
[b] Frequencies of 1670, 1715, and 1760 cm^{-1} were observed in the spectrum of pure acetic acid.
[c] Frequencies in the infrared spectrum are quoted.

Lascombe et al. [110] observed that acetic, propionic, valeric, hexanoic, and benzoic acids in butanol exhibit two frequencies (in particular the 1710 and 1754 cm^{-1} frequencies of acetic acid), which can be attributed to two types of complexes, the formation of which entails hydrogen bonding involving the carbonyl group (1710 cm^{-1}) and the hydroxy-group of the acids (1754 cm^{-1}), a change in the concentration from 10^{-2} M to 1 M being without effect on the observed bands. Izmailov and Kutsyna [121] observed the following changes in the Raman spectra of the same solutions (acetic acid in butanol) as the acid concentration was varied: at a concentration of 10 mole % they observed a single band at 1706 cm^{-1} which they assumed to correspond to addition products with the composition AB_2; at 20–40 mole % two frequencies were found at 1706 and 1736

cm^{-1}, the first being more intense than the second; in the spectrum of the solution at a concentration of 60 mole % three bands were observed at 1660, 1703, and 1745 cm^{-1}. The same frequencies also persist in the solution at a concentration of 80–90 mole % of the acid, the intensity of the line due to the dimer increasing continuously, which is evidence for the presence of dimeric acid molecules together with molecules linked to the solvent species. The authors assumed that in solutions of acetic, monochloroacetic, and trichloroacetic acids at low concentrations in water, methanol, or butanol the same addition products are formed since the same frequencies are observed in all these solutions: 1706 and 1710 cm^{-1} for acetic acid in alcohols and water and correspondingly at 1736 and 1728 cm^{-1} for monochloroacetic acid and 1760 and 1748 cm^{-1} for trichloroacetic acid.

Glagoleva and Ferkhlin[122] made a very thorough investigation over limited ranges of aqueous solutions of acetic acid at low concentrations. Their data demonstrate that in the presence of 33 wt. % of acid the carbonyl band is very pronounced and has a maximum at 1700 cm^{-1}. Bands are also observed at 1710 and 1680 cm^{-1}. At high dilutions, the band remains in the same position up to a concentration of 8.3 wt. % and then the maximum at 1700 cm^{-1} disappears, but the bands at 1690 and 1710 cm^{-1} persist down to an acid concentration of 1.3 wt. %. The appearance of a band at 1690 cm^{-1} is explained by the formation of hydrates. This may be evidence that the hydrogen bond between water molecules and the carbonyl group of the acid persist for a fairly long time despite the fact that at a concentration of 6.0 wt. % dissociation of the acid begins. These data suggest that solvates of several types exist in dilute solutions.

It is no less interesting to compare the data of Glagoleva and Ferkhlin[122] with those of Feneant[124] for high concentrations of the acid in the same system (both studies were based on Raman spectroscopy). According to Glagoleva and Ferkhlin[122], the band with the highest intensity is at 1700 cm^{-1} in the concentration range 87.0–63.0 wt. %, while at a concentration of 78.8 wt. % a new band appears at 1690 cm^{-1}; Glagoleva and also Izmailov and Kutsyna demonstrated the formation of monohydrates in the same concentration range. According to these authors, further dilution did not change the form of the band, but at concentrations of 62.8 and 65.0 wt. % of the acid the 1700 cm^{-1} band becomes sharper and narrower. The authors conclude that dihydrates are formed in this concentration range. However, according to Feneant[124], in the spectra of solutions at a concentration of 65 wt. % the band at 1715 cm^{-1} has the highest intensity and can be assigned to the dimeric monohydrate; on further dilution (63 wt. %) the same frequency remains the most intense and is interpreted by the authors as due to the dihydrate. According to the observations of the authors of both investigations, the band associated with the dimer disappears at these concentrations. The changes occurring in the solution are attributed to the formation of association complexes of several types.

The change in the contour of the stretching vibration band due to the C=O group in carboxylic acids on formation of an intermolecular hydrogen bond[104,107] is of considerable interest. Since the relations concerning the effect of adjacent atoms on the intensity and frequency of the C=O stretching vibrations in carboxylic acids are similar to those characteristic of ketones, the observed frequencies were assigned[123] by analogy with the C=O frequencies of ketones, in accordance with a number of investigations[114–116,125] and also in accordance with data on the stretching vibrations of the carbonyl group of acids in solvents of different types[19–21,55–57,100,106–117,110,121,122,124,126]. The spectrum of an equimolar mixture of propionic acid and water[123] (Table 1) has a characteristic band at 1723 cm^{-1} and a shoulder at about 1708 cm^{-1} on its long-wavelength slope.

The presence of a single intense band suggests that a 1 : 1 addition product with the same composition is mainly formed in the solution. Very small amounts of acid dimers and solvates of the composition A_2B and AB persist in the solution, as shown by the weak band at 1750 cm^{-1}. The carbonyl group of the acid remains free in such complexes (A is the acid and B is water).

The study of the infrared spectra of homogeneous saturated water–monocarboxylic acid (propionic, valeric, oenanthic)–heptane systems[123] over a wide range of concentrations and analysis of the results led to the following postulates and conclusions. In solutions with a high molar content of the inert solvent (heptane) (5.70–4.20 M) acid concentrations in the range 0.7–0.9 M, and water concentrations in the range 0.04–0.10 M, similar C=O frequencies (1720–1725 cm^{-1}) are observed for all the systems. Probably open-chain acid dimers, undergoing O–H...O–H and O–H...O=C interactions with water molecules, are present in such solutions and the nature of the hydrogen bond in the addition products and the structure of the association complexes differ little.

In the spectra of solutions with high contents of acids (1.00–5.00 M) and water (0.5–3.0 M) absorption bands due to the C=O group appear at 1740–1745 cm^{-1}, which indicates the presence of addition products A_2B and AB containing free carbonyl groups.

In solutions with high acid (8.0–5.0 M) and water (0.6–7.0 M) concentrations differences are observed in the structure of the hydrates of the systems investigated[123]. Hydrates with the composition AB_2 (band at about 1690 cm^{-1}) are formed mainly in solutions with propionic acid and are present in insignificant concentrations in solutions of valeric and oenanthic acids. In highly concentrated solutions of the latter bands due to acid dimers and possibly free water molecules (1715 cm^{-1}) appear. Bands of this kind are absent from the spectra of propionic acid solutions. The spectra of the postulated complexes may be formulated more precisely by studying the spectra of solutions of the deuterated derivatives[126].

The changes in the intensity of the carbonyl band were investigated by Venograd and Spurr[127] and by Huggins and Pimentel[128]. The ratios of the integral absorption coefficients of the carbonyl bands of the acid dimers and monomers measured by Venograd and Spurr are 1.15 for acetic acid, 1.36 for propionic acid, 1.22 for benzoic acid, and 1.32 for toluic acid. When complex aggregates of associated molecules are formed, the interpretation of the intensities and the widths of the band becomes much more complicated. To account for the spectra of such complexes, it is necessary to take into consideration angular deformation vibrations. Huggins and Pimentel arrived at a similar conclusion[128] and separated hydrogen-bonded systems into two classes: in the first they included systems with hydrogen-bonded complexes and in the second systems with hydrogen-bonded polymers.

A simple relation was observed between the frequency shift and the intensity of absorption by hydrogen-bonded complexes. There is a linear hydrogen bond in the complexes. When bonds of this kind are formed, an increase in the intensity of the stretching vibration bands accompanies their frequency shift. The same workers showed that the intensity does not alter on formation of a

non-linear hydrogen bond. The decrease of the integral intensity of the C=O band with increasing concentrations of acid and water in the systems can probably be accounted for by the formation of a non-linear hydrogen bond in acid–water association complexes[123]. Such data lead to the conclusion that, when the system A–H...B deviates from linearity, the intensity of the bands associated with the stretching vibrations involved in the formation of hydrogen bonds does not increase.

Sokolov[86] showed that the spectroscopic effect of the hydrogen bond may be related to the proton transfer process and consequently to a change in acidity. The reason for the decrease of acidity in the homologous series of acids is a positive inductive effect[129]. A characteristic feature of the inductive effect is its rapid decay along the chain of single bonds, which is evident from the acid dissociation constants: 17.6×10^{-5} for formic acid, 1.76×10^{-5} for acetic acid, 1.34×10^{-5} for propionic acid, 1.50×10^{-5} for valeric acid, and 1.38×10^{-5} for heptanoic acid. On the other hand, the first ionisation potential of aliphatic acids[130] increases in the sequence $H < CH_3 < C_2H_5 < C_3H_7$: 11.33 eV for formic acid, 10.66 eV for acetic acid, 10.47 eV for propionic acid, and 10.22 eV for butyric acid.

The energy of the hydrogen bond formed by monocarboxylic acids depends on both factors and its constancy in the homologous series of acids (ΔH = 7.5–8.0 kcal mole^{-1}) implies that the increase of the electron-donor capacity of the C=O group is compensated by a decrease of the proton-donor capacity of the O–H group.

The systematic study of the spectroscopic effects of hydrogen bonds began with the work of Gordy and Stanford[131,132] and also Searles[133] and Tamres[134]. They established that the low-frequency shift of the A–H stretching vibration band on formation of a hydrogen bond increases linearly with the basicity of the solvent.

In their study of hydroxylated substances and proton-acceptor substances (acetone, acetophenone, cyclohexanone), Singul and Ignat'eva[135] drew attention to the frequency change observed in the vibration spectra of proton acceptors. They established an inverse correlation between the shift of the C=O band and the pK_a of the hydroxylated substances. The hydroxylated solvents used were the initial members of the homologous series of saturated monohydric alcohols ranging from methanol to butanol and water and phenol, the greatest C=O frequency shift being observed when the ketone interacts with phenol. Since a linear relation was obtained for each ketone, this also characterises the different basicities of the ketones investigated.

A direct correlation was established[135] between the change in the frequency of the C=O group of acetic acid and its substituted derivatives and also substituted benzoic acids on the one hand and the acid strength in alcohol solutions on the other. A similar relation was found[123] between the frequency of the carbonyl group in carboxylic acids, participating in the formation of an acid–water complex, and their acid strength in the aqueous solution.

The linear relation between the C=O frequency shift and the pK can be explained by the relations linking the acid strength and the frequency of the carbonyl group to its polarisation and therefore any intermolecular interaction which alters the bond polarisation leads to a change in both acid strength and the carbonyl frequency.

In many cases a correlation has been observed between the spectroscopic characteristics of the C=O group and the parameters of free molecules[93,115,116]. Denisov's studies[115] showed that for the systems ketone–acid there is a correlation between the shift of the carbonyl band of the ketone and its first ionisation potential. The latter can probably serve as a measure of the relative electron-donor capacity of the ketone. As in the ketone series, the variation of the relative shift of the carbonyl band with the first ionisation potential was observed in the series of esters[137]. However, in the case of the ester carbonyl band a larger carbonyl shift occurs over a smaller range of ionisation potentials, although esters are poorer proton acceptors[138] than ketones. Probably the C=O frequency shift can serve as a measure of electron-donor capacity only within an individual class of compounds.

A number of determinations of the dimerisation energy of carboxylic acids in the gas phase as the principal characteristic of the hydrogen bond have been made[112,139]. The energy of the hydrogen bond in dimerised monocarboxylic acids does not change in the gas phase either when the molecular weight increases or when the structure of the non-carboxy-residue is altered[111,140].

The energies of the hydrogen bonds of certain acids in carbon tetrachloride solutions have been determined in a number of investigations[141–144]. However, very few data characterising the strength of the hydrogen bond of carboxylic acids in different solvents have been published[107]. The energies of the hydrogen bond in carboxylic acids per O–H...O=C bond are listed in Table 2.

Table 2. Energies of formation of O–H...O=C hydrogen bonds according to spectroscopic data.

Acid	Medium	Energy, kcal mole^{-1}	References
From acetic to valeric	gas phase	2 (8—8.5)	112
Acetic	CCl_4	2 (5.38)	141
Acetic	CCl_4	2 (5.38)	139
Isobutyric	CCl_4	2 (5.5)	107
Benzoic	CCl_4	2 (5.25)	144
Benzoic*	CCl_4	2 (8.2)*; 2 (4.2)*	145, 146
Benzoic*	$CHCl_3$	2 (6.35)	145
Isobutyric	$CHCl_3$	2 (4.2)	107

*Data on the energy of the hydrogen bond obtained by Klages and Möhler[145].
**Data of Wall and Banes[146].

Comparison of the effects of various solvents on the energy of the hydrogen bond shows that, on transition from the gas phase to the solution, even in an inert solvent such as carbon tetrachloride, there is a considerable decrease of the hydrogen bond energy. The energy of the O–H...O=C bond for solutions of acids in chloroform is even lower. Probably a change in the solvent may alter the type of equilibrium (dimer ⇌ open chain dimer ⇌ monomer) and the relative content of the monomer. The presence of open-chain dimers of carboxylic acids can explain the discrepancy between the bond energies for gases and solutions in carbon tetrachloride. To account for the decreased hydrogen bonding in acids dissolved in chloroform compared with the solutions in carbon tetrachloride, it is suggested[107] that the complexes are formed via RC=O...$HCCl_3$ hydrogen bonds and the acid monomers interact with chloroform more strongly than with carbon tetrachloride.

In solutions in hydroxylated solvents it is possible to determine only the formation constant of the complex which yields information about the average energy of the hydrogen bond in the compound, while adequate data on the energy of the individual C=O...H–O bond cannot be obtained. Therefore it is impossible to compare the frequency of the C=O group bound in the complex with the energy of the corresponding hydrogen bond.

The dependence of the relative shift $\Delta\nu/\nu$ of the absorption bands due to the C=O groups in acid dimers and monomers on the universal interaction function $(n^2-1)(2n^2+1)$ makes it possible to assess the strength of the interaction between the components in solution[110,123]. The effect of solvents on the frequency of the C=O group of acid dimers differs appreciably from their effect on the C=O frequency of monomers. Regardless of the nature of the solvent, plots based on the Kirkwood–Bauer–Magat formula show that all the points corresponding to the C=O frequency of the dimers are distributed near a straight line, while those corresponding to the C=O frequencies of the monomers lie to the right of the theoretical straight line. The effect of the solvent on the dimer is smaller, since the dimer is a symmetrical complex with a dipole moment close to zero because its active polar groups C=O and O–H are hydrogen-bonded. On the other hand, the effect of the medium, which leads to a decrease of the potential energy, may be regarded as a consequence of the interaction of the acid molecules with one or several of the surrounding solvent molecules.

Thus we have examined the results of many investigations[55-57,106-108,110,115-117,123,126] devoted to the effect of the hydrogen bond on the absorption bands of proton-acceptor groups in the infrared and Raman spectra. These data show that the band due to the stretching vibrations of the C=O group in ketones and monocarboxylic acids is sensitive to association and the formation of a hydrogen bond, while the change in the contour of the band due to the C=O group in carboxylic acids on formation of an intermolecular bond yields data on the immediate environment of the carboxy-group.

The increase in the number of observed bands in the region of the C=O stretching vibrations of carboxylic acids is evidence of the formation of different types of association complexes (dimer, open-chain dimer, compounds with the composition AB, A_2B, AB_2). The presence of different types of association complexes has been established on the basis of the temperature[104,107] or concentration[55-57,107,110,115-117,120-123,126] variation of the band positions. In many cases it is possible to determine the type of the association complexes in the systems by simultaneous application of infrared and Raman spectroscopic methods together with physicochemical methods[34,36,40-53,121-123].

Studies of the effect of the hydrogen bond on the infrared absorption spectra due to the stretching vibrations of proton-acceptor groups have been made only in recent years; the general form of the relation governing the force constants of such systems has not yet been elucidated. Its elucidation will provide new information about the structure of the complexes formed in the systems.

Summarising, it is noteworthy that the study of the physicochemical and spectroscopic characteristics of associated compounds and their solutions indicates a wide variety of intermolecular interactions in solutions. Comprehensive studies of the properties of a definite group of substances and the discovery of special relations will in future contribute to a general and unique solution theory.

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