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RELATIONSHIP BETWEEN THE ELECTRON-SHARING ABILITY OF RADICALS AND THE IONIZING POWER OF NON-AQUEOUS SOLVENTS

by

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TABLE OF CONTENTS

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INTRODUCTION

Numerous studies have been made in attempts to find an activity series of organic radicals which would enable chemists to predict the physical and chemical properties of compounds containing these radicals. In the first of a series of papers attacking this problem, Hixon and Johns (30) made the statement, "If the electron theory of valence holds, then the properties of any series of compounds such as ROH, RCOOH, RCH_2COOH, RCH_2CH_2COOH, RNH_2, RSH, $RAsO(OH)_2$, etc., must be a function of the 'electron-sharing ability' of R if we exclude from consideration under R all groupings which themselves have polar linkages." By reference to the tables compiled in Landolt-Börnstein (41), these investigators demonstrated that one series of radicals was sufficient to show the variations in acidity of all the types of compounds listed above, using as a criterion the dissociation constants of these compounds in water. This series had an arbitrary scale of units, based on the assignment to hydrogen of a value of zero. Those radicals which, when substituted for hydrogen in an acid, cause its dissociation to increase are said to have positive electron-sharing ability. Examples are C_6H_5-, $\alpha-C_{10}H_7-$ and halogens. Conversely, those radicals which, when so substituted, cause a decrease in acid strength are said to have negative electron-sharing ability. Alkyl radicals are of this type.

The term electron-sharing ability is, no doubt, a rather comprehensive one, embodying many individual contributing effects, but it is maintained that the electron-sharing ability of a radical is a property of that radical, to which each of the several individual effects contributes in about the same proportion under varied sets of conditions. This has been shown to have at least a pragmatic basis in truth. If the ionization of an acid, a reversible reaction, depends upon the electron-sharing abilities of the radicals attached to the carboxyl group, then this same property of the radicals should govern the behavior of their compounds in other reversible reactions. This has been found to be true in the studies made thus far, among which may be cited work on the reversible condensations of mercaptans with chloral (32), the reversible splitting of organomercury compounds (33) and organomercuric cyanides (9) and the extensive studies by Landee on the association of organic compounds, both in the vapor state and in solution (40).

Other applications of this concept include studies on the dissociation constants in water of the α-substituted pyrrolines (63)(38), the N-substituted pyrrolines and the

α-substituted pyrrolidines (11)(38), and also on the dissociation constants in ethanol and in methanol of the above types (23). Similar studies have been made of the α-substituted tetrahydroquinolines (57).

Further studies have made application of this concept to the variations of refractive indices of organic compounds with substitution (8), the variations in optical activity of organic compounds with substitution (52), and the displacement in Raman frequencies with radicals of varying electron-sharing abilities attached to the bond emitting the radiation (47).

It was the purpose of the present study to apply, if possible, this concept to a study of the role played by the solvent in the process of electrolytic dissociation. More precisely, this study was concerned with the effect of radicals of varying electron-sharing ability attached to the functional group of a solvent molecule on the ionizing power of the solvent.

HISTORICAL AND THEORETICAL

The process of electrolytic dissociation and the factors affecting it have been the subject of innumerable investigations since 1883 when Arrhenius published his classic paper in this field. The broad outline of developments in this field is familiar to all chemists and will be reviewed here only briefly.

Arrhenius believed that electrolytes were mixtures of "active" and "inactive" molecules. When the electrolyte was dissolved in water, the "active" molecules, a considerable fraction of the whole, dissociated into electrically charged particles, which he called "ions". In this way he explained the conduction of an electric current by such solutions, the ions being drawn toward the electrode of opposite sign by the influence of its electrical field. Arrhenius recognised that the proportion of "active" to "inactive" molecules varied with the concentration.

In 1885, van't Hoff read a paper before the Swedish Academy of Sciences in which he showed the gas laws to be applicable to dilute solutions. However, some of his data did not conform to this rule. In order to make these solutions, in which the solutes were acids, bases or salts, conform to his rule he introduced a corrective factor which has come to be known as van't Hoff's "i". This paper was published two years later (67). Arrhenius saw the significance of the "i" factor in the light of his own theories (3). He was able to calculate it from his conductance measurements, as well as from the cryoscopic and osmotic pressure measurements used by van't Hoff. This confirmation lent much support to Arrhenius' theory of electrolytic dissociation.

The Arrhenius electrolytic dissociation theory met with stubborn opposition, chiefly because it forced a considerable revision of the scientific thought of the day, and because there was no physical evidence for the existence of the ions. Nevertheless, it gradually gained acceptance over a period of controversy lasting for thirty years. His main idea, that of spontaneous dissociation of electrolytes in solution, is now accepted almost universally, and Arrhenius' theory is even now regarded as being almost entirely correct in the cases of solutions of weak acids and bases.

As work in this field progressed, a number of data were obtained which could not be accounted for in terms of the Arrhenius theory. Most of these data were obtained by conductance measurements and concerned the solutions of strong electrolytes. Such solutions did not obey the law of mass action nor Ostwald's dilution law. Many empirical formulae and corrective factors were proposed for correcting these discrepancies, among which the activity concept of Lewis may be mentioned as most prominent (44).

Although satisfactory from an experimental viewpoint, none of these methods explained the deviations, and gradually new theories were developed concerning the solutions of strong electrolytes, the most successful of which has been the Debye-Hückel theory of complete dissociation. The idea of complete dissociation had been advanced in a qualitative way as early as 1904, by Lewis (45) and Noyes (56), among others. In 1915, the work of W. H. and W. L. Bragg (5) on the structures of the alkali halide crystals, which revealed these structures as ionic rather than molecular lattices, lent plausibility to these rather dubiously received views and gave impetus to the idea of complete dissociation.

Among those who developed the earlier quantitative treatments of this concept may be mentioned Milner (48) and Ghosh (21). Milner's mathematical treatment was quite complicated and, perhaps for this reason, his ideas failed to attract much attention. Ghosh treated the subject in a much simpler fashion mathematically, but his ideas were not well received, it being claimed that many of his assumptions were invalid.

In 1923, Debye and Hückel presented their now familiar "ionic cloud" theory (12). This postulate stated that electrolytes in solution were completely dissociated, and that each ion was surrounded by an atmosphere or cloud of other ions. This ionic cloud contained an excess of ions possessing a charge opposite in sign from that of the central ion. When an ion is drawn toward an electrode, it must be pulled in that direction against the attraction of its ionic atmosphere. The variation of conductance with concentration is assumed to be due to changes in ionic mobilities. These, in turn, are determined by the nature of the ionic atmosphere surrounding the central ion. For instance, if the solution is diluted, the ionic cloud becomes less dense, the interionic attraction is lessened, and hence ionic mobility (and conductance) increases. If the concentration is increased the interionic attraction is also increased, and conductance decreased. In general, the theory of Debye and Hückel has proven itself quite satisfactory in the treatment of dilute solutions of strong electrolytes, not only in aqueous, but in many non-aqueous solvents. The great bulk of the recent work in the field of conductance interprets data in the light of this theory for both types of solutions.

It is in the field of non-aqueous solutions where deviations from this theory occur most frequently. Among the several investigators reporting such divergences from the theory may be mentioned Hartley and Bell (28), Ferguson and

Vogel (17), and Hawkins and Partington (29). Nernst (53) together with Orthman (55) has attempted to show that these deviations are due to the presence, even in dilute solutions of strong electrolytes, of small amounts of unionized molecules whose equilibrium with their ions would be in accordance with the law of mass action. If this were true, such a solution could not be expected to follow strictly the equations of Debye and Hückel, since the first assumption of their theory, that of complete ionization of the electrolyte, would be invalid.

The role played by the solvent in the process of electrolytic dissociation has been comparatively neglected until recent years, and no satisfactorily comprehensive explanation of the part it plays in the dissociation process has yet been advanced. This is due largely to the excellent solvent properties of water, which, together with its cheapness and universal availability, has virtually tied the development of chemistry to systems based on water as a solvent. An examination of one of the few exceptions to this trend, Franklin's development of the ammonia system of chemistry (18), indicates how much of theoretical interest has been missed by the close adherence of chemists to the water system of chemistry.

All previous developments in the study of solvent effect on electrolytic dissociation have been made in the field of non-aqueous solutions, and it is to this same type of solutions to which we must look for developments in the future.

Among the earlier workers in this field, Dutoit and Aston (14) stated that a solvent possessed ionizing power only if it was associated in the liquid state. This view was disproved by Walden (70) who showed that all solvents were capable of causing ionization to some extent.

Most interpretations of solvent action have been made in the light of the Nernst-Thomson rule. This rule is merely the application, to the dissociation process, of a principle discovered by Faraday (16). This principle states that the force between two electric charges depends not only on the distance between them, but also on the dielectric constant of the medium. It may be expressed mathematically as follows:

$$F = \frac{q_1 q_2}{D\ d^2}$$

where "F" is the force between two charges "q_1" and "q_2", separated by a distance "d" in a medium of dielectric constant "D". It is obvious that for any given distance, the force between the charges will be less, the greater the dielectric constant. In a general way, the greater the dielectric constant of a solvent, the greater is its ionising power. This fact seems to have been first noticed at about the same time by Nernst (54) and Thomson (64) and formulated into the rule which bears their names.

Nevertheless, the ionizing power of solvents cannot be explained solely in terms of their dielectric constants. There are many deviations from this rule, some of which are very marked. The work of Fredenhagen and Dahmlos (19) furnishes an example. Their results, based on conductance measurements, indicated that hydrocyanic acid possessed much less ionizing power than did water although the dielectric constant of hydrocyanic acid is considerably higher than that of water (hydrocyanic acid, 96; water, 81). Numerous other exceptions have been noted in the field of non-aqueous solutions. The fact that other effects beside that of the dielectric constant must be considered in accounting for ionizing power has been recognized for many years. Long ago, Sachanoff (60) and Plotnikoff (59) pointed out that when the dielectric constant of a solvent is small, its chemical constitution becomes the principal factor in determining its ionizing power.

More recently, Kendall and Gross (37) stated that ionization was dependent on preliminary compound formation between solvent and solute, as represented by the following general reaction.

$$A^+B^- + CD \rightleftharpoons ABCD$$

Once the intermediate is formed the degree of dissociation depends upon the relative extents of the two dissociations of the intermediate, either back into the original components or into ions. This reaction is represented in general form by the following equation.

$$A^{+}B^{-} + CD \rightleftharpoons ABCD \rightleftharpoons A^{+} + BCD^{-}$$

These investigators presented data concerning the stability of the intermediates with regard to their original components, showing that they are more and more stable as the acidity and basicity of the solute and solvent, respectively (or vice versa), become more and more diverse. A strong acid and a strongly basic solvent form a stable intermediate, whereas no intermediate is detected in a system containing a weak acid and a more or less neutral solvent. These systems were studied cryoscopically and the data interpreted by means of phase diagrams. By measuring these same systems conductimetrically, they came to the conclusion that, in a general way, the greater the amount of intermediate formation, the greater was the ionization in the system.

This view is by no means original with these authors, having been held for years previously by most of those chemists who could not reconcile themselves to a purely mechanical concept of ionization. Kendall et al. (36) have summarized the work of earlier investigators in this field and presented a discussion of the mechanism for ionization via intermediate formation.

Hunt and Briscoe (31) proposed to correlate and to explain the three closely related properties of a solvent--

its ionizing power, dielectric constant, and association--in terms of a more basic concept, its electronic structure. They supported Kendall's ideas of intermediate formation between solute and solvent, which they attributed to the formation of coordinate-covalent bonds between the two. They pointed out that as the solvent is made more basic by the introduction into its molecule of so-called "electropositive groups," its ability to form bonds of this type should be likewise increased. The ionization of an acid should increase under these conditions, because the solvent molecule would have more attraction for the proton. "Electronegative groups" should have an opposite effect. Hunt and Briscoe found few data to support these postulates. Few data applicable to a test of these ideas are available in the literature, even data of a qualitative nature.

Mention should be made here of the work of Hantzsch (27), who published a series of papers on the variation of acidity of an acid with change in the solvent. His data were obtained by comparison of indicator changes and by kinetic studies, particularly the decomposition of diazoacetic ester, an acid-catalyzed reaction. Hantzsch's ideas appear at first glance to be widely at variance with those of his contemporaries, but a closer inspection shows these apparent discordancies to be due to Hantzsch's definition of acidity, which is not based on ionization as is usual.

According to Hantzsch's terminology, a solution is acid when the protons are insecurely held. Hence, a solution of perchloric acid in chloroform is very strongly "acid", since neither the solvent molecule nor the acid anion holds the proton very firmly. By the same token, a solution of perchloric acid in water, at the same concentration, would be much less "acid" because it is largely ionized; here the proton is rather firmly held by the solvent in the form of oxonium ions. Hantzsch's findings offer no opposition to a concept of acidity based on ionization and agree in a general way with the ideas of Hunt, Briscoe and Kendall. Hantzsch's results are supported by those of Conant and Hall (10), and his ideas have been summarized by Hammett (25).

The process of electrolytic dissociation, particularly in regard to the role played by the solvent, has been considerably clarified by the theories put forth by Brönsted (7) and Lowry (46) in their numerous publications, and by their followers in this field. For those interested in a detailed perusal of the work in the development and application of these theories, a bibliography of eighty-two references (including eighteen reviews) selected from among the four hundred odd papers in this field has been compiled by Alyea (2). The various theories of acid-base systems from Lavoisier's oxygen concept to the most modern ideas on this subject, including, as well as the Brönsted-Lowry system, the more general ideas of G. N. Lewis (43) and of Usanovich (66), have been reviewed recently by Hall (24).

Brönsted's ideas are familiar to all chemists and will be reviewed here only insofar as they apply to the problem at hand. Brönsted recognized that acids and bases are essentially different from salts. The latter, as shown by the work of W. H. and W. L. Bragg, are ion aggregates, and their behavior in solution is best dealt with in physical terms as in the theories of Debye and Hückel. Acids and bases, on the other hand, are characterized by proton exchange as represented by the following general reaction.

$$\text{Acid} \rightleftharpoons \text{Base} + \text{Proton}$$

In the Brönsted system an acid is any substance which can give up protons; a base, any substance which can accept them. Both acids and bases may be either uncharged molecules or ions.

In a formal sense this system is independent of any solvent, but it embraces in a general way the action of all solvents. It has been shown that the above reaction can take place to a measurable extent only when two competing proton acceptors are present. Thus the reaction is always at least as complicated as the following:

$$\text{Acid}_1 + \text{Base}_1 \rightleftharpoons \text{Acid}_2 + \text{Base}_2$$

In the case of ionization, the two competing proton acceptors are the solvent and the acid anion, the general reaction being as follows:

$$\text{Acid} + \text{Solvent} \rightleftharpoons \text{Solvated Proton} + \text{Base}$$

There are thought to be practically no free protons in a solution of an acid.

The factors affecting a change in ionization of this type due to a change in solvents have been summarized by Wynne-Jones (74), and they are three:

(1) The chemical potentials of the acid and base (acid anion) may vary with changes in the solvent.

(2) The electrostatic attraction between the solvated proton and the acid anion varies with different solvents.

(3) The basicity of different solvents varies.

The contribution of the first of these factors is difficult to estimate. It has been suggested by Bjerrum and Larson (4) that, since the acid and base differ only by a proton, the variations in chemical potential of the two may be assumed to be independent of the solvent.

The second of these factors, since it deals with the force between two separate electrical charges, should obviously be a function of the dielectric constant of the medium. Wynne-Jones made calculations on available data which indicated that this was the case. Taking one acid as a standard (benzoic acid), he compared the strengths of other acids with it in each solvent considered, taking as criteria the dissociation constants of the acids. He thus obtained a value K_r, the ratio of the dissociation constant of the standard acid to that of the other acid in the solvent under consideration. He then made calculations indicating that when the solvent was changed, the change in log K_r should be a linear function of the change in the reciprocal of the dielectric constant of the solvents in question. Then, for a series of related solvents (sufficient data were available only in the solvents ethanol, methanol and water), he plotted log K_r against the reciprocal of the dielectric constants and obtained straight lines for a large number of acids of all types. By extrapolation to the log K_r axis (1/D equals zero, and hence D equals infinity) he got a ratio which he called a ratio of the "intrinsic strengths" of the two acids (the ratio of the two acid strengths in a medium of infinite dielectric constant). This he proposed to use as a basis for comparison of acid strengths, hoping thus to evolve an order which would be independent of any solvent.

It should be noted in this connection that Wynne-Jones made the tacit assumption that the varying basicity factors of these different solvents affect all acids concerned in the same proportion. Whether or not this assumption is valid remains to be proven since there were not enough data available to show whether or not the "intrinsic strengths" of the acids are independent of the type of solvent. In the light of the theories of Hixon and Johns, it may be seen that the change in the electron-sharing abilities of the radicals involved in this solvent series is in the same order, and of approximately the same relative magnitude, as the change in the reciprocals of the dielectric constants. Thus any changes in basicity effects might be expected to parallel the changes due to dielectric effects, so that the former effect would also be included in the curve. Obviously, whether or not this is so cannot be said without more data for different solvent types.

It was the last of the three factors summarized by Wynne-Jones with which this study was concerned. The importance of the basicity of the solvent as a factor in determining its ionizing power has been stressed, at least in a qualitative way, by numerous investigators among whom may be mentioned Kendall and Gross (37), Conant and Hall (10), Brönsted (6), Hunt and Briscoe (31), Hammett and Dietz (26), and Schwarzenbach (61).

Quantitative measurements of this effect, which might give some indication as to its nature, have not been forthcoming. There are several difficulties inherent in such measurements. First, in order that the solute should not be an ion lattice, and hence subject to treatments of the type of Debye and Hückel, we are limited to the weak acids and bases. Thus we are forced to make measurements on the ionization of weak electrolytes in solution in solvents possessing much less ionizing power than does water. Such measurements are subject to considerable difficulty.

Second, measurements of this effect are complicated by the fact that once ionization takes place to any considerable extent, we are dealing with free and separate electrical charges, and variant dielectric effects of the different solvents will cause the electrostatic attraction between the free ions to vary. This effect will, of course, be included in the ionization constants which we shall take as criteria of the ionizing power of the solvents. If the dielectric effects become too variant they might conceivably mask the basicity effects with which this study is primarily concerned.

Finally, it was only recently that there was made available a suitable scale for the measurement of the electronic properties of radicals, which the author hoped to show as determining, at least in part, the basicity properties of solvents. Due to the work of Hixon, Johns, et al., such a scale is now available, and it was hoped that, by using suitable precautions, measurements of sufficient accuracy to show the relation between the electronic properties of radicals attached to the functional group in a solvent molecule and the basicity of that solvent might be made.

Returning to the ideas presented above in the brief discussion of Brönsted's contributions and selecting a ketone as an example of a solvent, we may represent the ionization of an acid as follows:

$$H:\underset{..}{\ddot{A}}: + R:\underset{:\ddot{O}:}{C}:R \rightleftharpoons :\underset{..}{\ddot{A}}:H:\ddot{O}::\overset{R}{\underset{R}{C}} \rightleftharpoons H:\ddot{O}::\overset{R}{\underset{R}{C}}{}^{+} + :\underset{..}{\ddot{A}}:^{-}$$

If we interpret the basicity of a solvent as meaning its ability to donate a pair of electrons to the hydrogen atom forming a coordinate-covalent bond, as suggested by Hunt and Briscoe, an idea which seems likely to the writer, it must be obvious that this basicity will depend on the electronic properties of the two R groups. By the definition of electron-sharing ability, if these two groups are groups of positive electron-sharing ability, they will tend to draw electrons toward themselves and away from the carbonyl carbon atom to which they are attached. This will tend to draw the electrons in the carbon-oxygen double bond toward the carbon atom and away from the oxygen atom, tightening the oxygen atom's electron octet, restricting its donor power and lessening its ability to form the intermediate. Groups of negative electron-sharing ability would tend to release electrons toward the carbonyl carbon atom, eventually increasing the donor power and power of intermediate formation of the carbonyl oxygen atom. This much has already been demonstrated by Landee (40) in connection with his studies on association (see effect of solvation thereon) and also in a qualitative way by the findings of Kendall, et al.

The intermediate so formed can dissociate in two ways, either into its original components or into ions. As pointed out by Landee, the dielectric constant of the solvent is a negligible factor in this process, as the bonds to be broken must be considered as being of the covalent type. Representing the acid anion by "A" and the solvent molecule by "S" the intermediate may be regarded as being made up, in the simplest case, of two resonating structures.

$$A \uparrow\downarrow H \qquad :S \rightleftharpoons A: \qquad H \uparrow\downarrow S$$

The arrows represent the opposite directions of spin of the electrons in the covalent bond. This reversal of forms has been estimated to occur at a rate of the order of 10^{15} times per second, far too rapidly for the bonds to be measurably affected by dielectric action. It is not possible to say at any time to which atom the hydrogen is actually attached (covalently), and in the light of the above structures both bonds must be regarded as being of the covalent type.

Thus, the prevailing direction of the dissociation of the intermediate will depend on the relative attractions, for the proton, of the acid anion and of the solvent molecule, a function of the tendency of the two competing bases to form a covalent bond, either normal or coordinate, with the proton. The attraction of the solvent molecule for the proton should be a function of the electron-sharing abilities of the R groups attached to the functional group in the solvent molecule. If R is a radical of negative electron-sharing ability, increasing the donor power of the donor atom of the functional group, the proton should be attracted to it as this bond will become relatively stable. In this case ionization will be comparatively large. Conversely, if R is a radical of positive electron-sharing ability, donor power in the functional group will be restricted, and the proton-solvent bond will be correspondingly weakened. Here the ionization would be comparatively small.

As mentioned above, once this first step in the ionization has taken place we are dealing with separate electrical charges, and the dielectric constant will become an important factor. Since the dielectric constant of the medium is an important contributing factor in determining the force between a pair of electrically charged particles, it will have a profound effect on the reverse reaction in the ionization process, the recombination of the ions to form molecules. This factor was necessarily included in the ionization constants which were taken as the criteria of ionizing power; hence certain precautions had to be observed in order to keep this complicating effect at a minimum.

An obvious precaution was to choose the solvents in any series so that there were no very large variations in dielectric constants among the individual members of the series. Thus it was hoped to keep this effect more or less constant for each series.

A more elegant modification of this method suggests itself but is limited to certain types of measurements. If the acid chosen is a cation acid, such as the ammonium ion, the acid ionization would be as follows:

$$NH_4^+ + S \rightleftharpoons HS^+ + NH_3{}^*$$

Since all ions present are of the same sign, the dielectric constant of the medium would have no effect, be it large or small. This method is suitable for potentiometric measurements, but for cryoscopic or conductimetric measurements, which were used in this study, this ionization is hopelessly complicated by the primary ionization of the ammonium salt.

A second, equally obvious, precaution was to choose an electrolyte which would not be ionised to any very great extent in the solvent, so that most of the solute was present

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*S represents a solvent molecule.

in the form of uncharged molecules. There is a practical limit to this however. If the ionization is too small, the experimental error will become too large for the results to have any meaning.

A third precaution, not so obvious on casual examination, was based on recognition of the fact that the basicity of an organic solvent must be divided into two or more factors. The first of these is the basicity inherent in the functional group of that solvent type. Some functional groups, such as the hydroxyl group, are inherently much more basic than others, such as the functional group in ethers, to cite more or less extreme differences. The contention of this thesis is that a second factor affecting the basicity of a solvent is the nature of the radicals attached to the functional group. Now, if the solvent series is one having functional groups of inherently high basicity, such as the alcohols, then no matter what radicals are attached to the functional group, all members of the solvent series may be expected to have a fairly high basicity. Further, since all members would have a high basicity, the variations in basicity with variation of radicals attached to the functional group would be small in comparison with the total basicity, so that effects due to varying the radicals attached to the functional group would be small and easily masked by other effects, in particular those due to differences in dielectric constant.

It is the belief of the author that this accounts for the fact that acids are generally ionized to a greater extent in methanol than in ethanol. According to the different basicity effects due to different radicals attached to the functional group, the ethanol should have the greater ionizing power, as the ethyl radical possesses a smaller electron-sharing ability than does the methyl radical. In the light of the above considerations, it may be seen that, while there may be some difference in the basicities of these solvents, the basicities of both of them would be quite large due to the high basicity inherent in the hydroxyl group and the difference would not likely be very large. There is, on the other hand, a very respectable difference in the dielectric constants of these two (methanol, 33.7; ethanol, 25.8), and this might be expected to overshadow completely the other, much smaller, effect.

A third factor, which we might expect to modify the basicity inherent in the functional group of a solvent, is the degree of association of that solvent. Generally, the solvents which have a high degree of ionizing power are associated in the liquid state. Many investigators have pointed out this fact and stated that the greater the association, the greater was the ionizing power of the solvent. The work of Landee has established the connection between association due to hydrogen-bridge formation and the electron-sharing ability of a radical attached to the functional group involved in the association. His findings showed that as the electron-sharing abilities of such groups became more and more negative the association increased. It will be remembered that in the previous discussion it was pointed out that, other things being equal, the ionization of a weak electrolyte in such a series of solvents should likewise increase as the radicals attached to the functional group became more and more negative as regards their electron-sharing ability. Whether the two effects are one and the same or if one of these effects reenforces, or conflicts with, the other cannot be said at present.

Thus it was apparent that solvents must be chosen so that their functional groups would have neither too high nor too low an inherent basicity. This must, of course, be established by trial and error. In addition to this, it was found necessary to use solvents having high enough dielectric constants to allow a reasonable amount of ionization so as to keep the experimental error within bounds. Further, it would have been ideal if the solvent series had been one in which association due to hydrogen-bonding did not take place, but this was a practical impossibility; all of the solvent series actually used showed this phenomenon for at least part of their members.

Thus, it was the opinion of this author that the electron-sharing abilities of radicals attached to the functional group in a solvent molecule were of primary importance in determining the basicity of that solvent, subject to the conditions mentioned above. It was hoped that, by observing the precautions given above, measurements of sufficient accuracy to test this hypothesis might be made, and it was toward that end that this investigation was directed.

A survey of the literature revealed no data extensive enough to constitute either a proof or a refutation of these ideas. This lack is due, at least in part, to the slight ionizing power of most non-aqueous solvents. This has restricted the great bulk of such work to a relatively few non-aqueous solvents. Ammonia and amines have been employed in many investigations, but the basicities inherent in the functional groups of these substances is too high for application to the present problem. Alcohols have been much used also, but here work has been done chiefly in ethanol and methanol. These are open to the same objection as the amines in regard to their basicities. In any case, these two do not form a solvent series giving a representative variation in electron-sharing abilities of radicals attached to the functional groups.

Other solvents on which considerable amounts of work have been done, chiefly in the field of conductance measurements, are acetone, formic acid and formamide, acetonitrile and benzonitrile, considering here only the organic solvents.

Most of the work on ionization in non-aqueous solvents is based on conductance measurements. Unfortunately for this study, almost all of this earlier work has been done using as solutes the strong electrolytes. Since these are ion-aggregates, one might expect the behavior of their solutions to be best interpreted in terms of the theories of Debye and Hückel. This appears, in general, to be the case. Many data of this type are tabulated in Landolt-Börnstein (41) and in the books of Kraus (39) and Walden (68). Some data of a qualitative nature are reported in Scudder (62).

The experimental part of this thesis will be divided into two sections, according to the two different methods used in making the measurements. The first part will deal with measurements made cryoscopically, and the second will deal with conductance measurements. The results obtained in each section of the work will be discussed at the end of that section.

PART I: CRYOSCOPIC MEASUREMENTS

EXPERIMENTAL

Apparatus

The apparatus for making determinations by the cryoscopic method is shown in Figure 1. The thermometers used in determining temperatures in the melt (A) were graduated in tenths of a degree Centigrade. There were two of these, one having a range of from minus twenty to fifty degrees, and the other a range of from minus ten to one hundred degrees. All readings were made with the aid of a thermometer reader, not shown in Figure 1. In this way it was possible to make readings with an accuracy of about one one-hundredth of a degree. A second thermometer (B) was suspended in the bath so that bath conditions could be duplicated on successive runs. This thermometer was graduated in degrees Centigrade and had a range of from minus twenty to one hundred twenty degrees. The bath (C) was a five hundred ml. beaker, filled with water. It was found that the rate of stirring of the water in this bath must be fairly rapid, and for this purpose a compressed air stirrer (D) was placed in the bath. The container for the melt was a large Pyrex test tube (E). Vigorous stirring of the melt is necessary

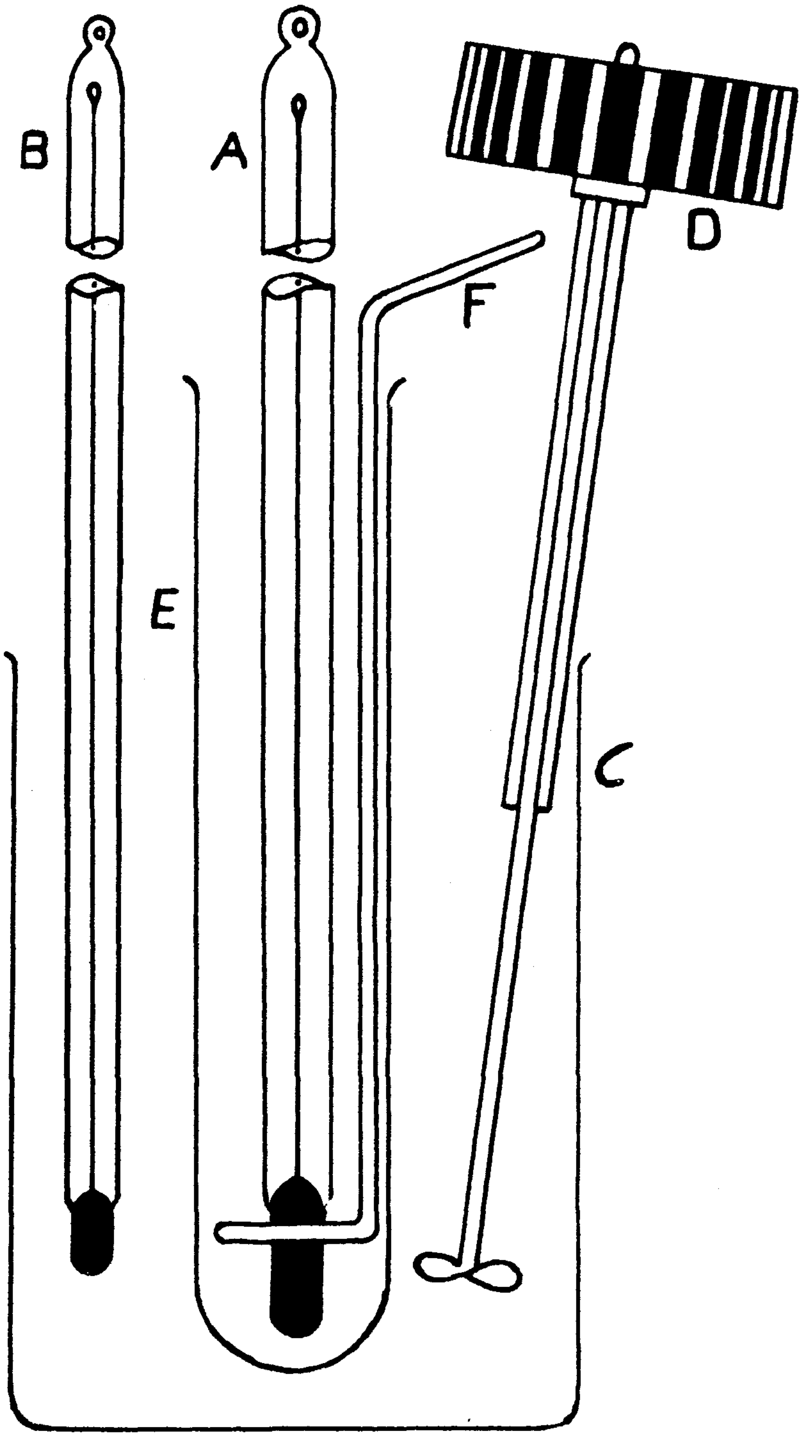


Figure 1. Apparatus for Freezing Point Measurements

if consistent results are to be obtained and this was accomplished by means of the glass rod-and-loop device (F).

Technique

Preliminary investigations on benzophenone showed that reproducible melting points could be obtained only by melting the mixture and taking its freezing point as the bath was allowed to cool around it. Constant and rapid stirring of both bath and melt is absolutely necessary if reproducible results are to be obtained. The temperature first drops below the melting point, even in the presence of the solid phase; then, as crystallization becomes more rapid, the melt temperature rises to a constant value which is taken to be the melting point. Since bath conditions influence the actual value obtained, if they are very widely variant, it was necessary to keep these conditions the same throughout any run. For those solvents which melted above room temperature, it was the practice to raise the bath temperature above the melting point, let the mixture melt, and then allow the bath to cool naturally. When the bath temperature reached the melting point the melt was seeded, and during all parts of the cooling period constant stirring of the melt was maintained. For those solvents which melted below room temperature, the practice was to cool the bath to about one degree below the melting point, then seed the melt to induce crystallization and to maintain stirring of the melt throughout the course of the determination.

By control of the bath conditions in this way, it was possible to obtain about the same degree of supercooling on successive determinations. All of the solvents used showed a marked tendency to supercool, even in the presence of considerable amounts of the solid phase. The practice of seeding the melt, together with vigorous stirring of both the bath and the melt, brought this potential source of error under control.

As a usual thing, melting point determinations were repeated until three successive readings checked each other within one one-hundredth degree. In those cases where such precision could not be obtained, final readings were the averaged results of five or six of the variant values whose mean range of deviation did not exceed five one-hundredths of a degree. The chief offenders in this respect were phenyl p-tolyl ketone and desoxybenzoin, the latter in particular. This was attributed to their extremely slow rates of crystallization, which greatly magnified the errors due to uneven bath conditions and stirring of the melt. In the case of determinations in desoxybenzoin, the melting points were so erratic that determinations in this solvent were finally abandoned altogether. While a cryoscopic constant for this solvent was obtained and is reported in Table 1, it must be regarded as being of very dubious worth.

Determination of Cryoscopic Constants

The solute used for the determination of the cryoscopic constants was naphthalene. The naphthalene used was Baker's C. P. grade (melting point, seventy-nine degrees). It was used without further purification.

Both solute and solvent were weighed on the analytical balance, the solute to the usual four places and the solvent to only three places. It is interesting to note that much difficulty was experienced in obtaining the melting points of some of these solvents in the pure state. However, if a small amount of naphthalene was added, the melting points became quite reproducible; this was done in the cases of propiophenone and phenyl p-tolyl ketone. Then larger amounts of naphthalene were added and the cryoscopic constant calculated from the temperature drop between the two reproducible melting points.

The cryoscopic constants were calculated by means of the usual equation,

$$(1) \qquad K = \frac{\Delta T_f \cdot G \cdot m}{1000g},$$

where:

K_f = the cryoscopic constant

ΔT_f = the freezing point depression in degrees Centigrade

G = the weight of the solvent in grams

m = the molecular weight of the solute

g = the weight, in grams, of the solute.

Since the values of the cryoscopic constant decreased as the concentration increased, it was the practice to keep the molar concentrations of naphthalene about the same in determining the constant as the concentrations of electrolyte to be used later on. It was thought better to keep the concentrations of reference solute and ionizing solute about the same, rather than to extrapolate the constants back to their values at zero concentration, since the deviations of activities from concentrations should be approximately the same for both the reference solute and the ionizing solute.

The maximum concentration of the electrolyte in these solutions was about one-tenth molal. Working in this concentration range with naphthalene as solute gives rather small values for the freezing point depression (of the order of one-half a degree), but the error in reading can be compensated to a large extent by determining two or three values for the constant and averaging them. In this way it was possible to check fairly closely the values reported by previous investigators, where such values were available.

Preparation and Purification of Materials

The solvents used in this part of the study were ketones of the type $RCOC_6H_5$. They were chosen, first, because the various members of the series melted in a range from fifteen to fifty-five degrees Centigrade, a convenient range for measurements of this type, and second, because previous work (40) had demonstrated that association in ketones was not large.

The individual members of the solvent series employed were acetophenone, propiophenone, benzophenone, phenyl p-tolyl ketone and desoxybenzoin. Their freezing point constants are tabulated in Table 1. Other relevant physical constants of these solvents are presented in Table 2.

Acetophenone (Eastman) was purified by distillation under reduced pressure. It was a water-white liquid, boiling at ninety-seven degrees under a pressure of twenty-two mm. of mercury. Its melting point was nineteen and thirty-three hundredths degrees Centigrade, as taken on the cryoscopic apparatus.

Benzophenone (Eastman) was used in these determinations without further purification. Its melting point (capillary) was forty-eight degrees Centigrade.

Propiophenone (Eastman) was purified by distilling in an atmosphere of purified nitrogen at reduced pressure. It was a colorless liquid, boiling at one hundred eight degrees

TABLE 1

Cryoscopic Constants of Ketones of the Type $RCOC_6H_5$

Substances	Author's value for Kf	Comparative value
Acetophenone	5.55	5.65 (20)
Benzophenone	9.86	9.88 (15)
Desoxybenzoin	9.30	None reported
Phenyl p-tolyl ketone	9.58	None reported
Propiophenone	5.55	None reported

TABLE 2

Physical Constants of Ketones of the Type $RCOC_6H_5$

Substances	E.S.A. of R.	Freezing point	Dielectric constant
Acetophenone	-1.45	19.35°C.	18.1 at 20°C. (69)
Benzophenone	4.2	47.67°C.	12.4 at 40°C. 11.4 at 60°C. (71)
Phenyl p-tolyl ketone	2.9	51.75°C.	None reported
Propiophenone	-1.80	15.43°C.	15.5 at 17°C. (13)

at a pressure of ten mm. of mercury.

Desoxybenzoin was prepared by the Friedel and Crafts reaction, according to the directions of Allen and Barker (1). Phenylacetic acid was converted to the corresponding acyl chloride with phosphorus trichloride. The reaction mixture was dissolved in benzene and filtered to remove phosphorous acid. The catalyst was added in small amounts to this solution. Following this, the solution was refluxed for two and one-half hours and hydrolyzed by pouring it over a mixture of ice and hydrochloric acid. Excess benzene was removed by distillation on the water bath and the product distilled under reduced pressure. The boiling point was one hundred ninety-five degrees at a pressure of thirty mm. The product was purified by recrystallization from methanol and melted at fifty-four degrees Centigrade. It was identified as the semicarbazone, melting point one hundred forty-five degrees (Beilstein, one hundred forty-seven degrees). The yield was forty-three per cent of the theoretical, based on the phenylacetic acid.

Phenyl *p*-tolyl ketone was prepared by the reaction of a Grignard reagent on a nitrile. The Grignard reagent was prepared by treating three-fourths of a mole of *p*-bromotoluene, in ether solution, with a slight excess of magnesium turnings. Benzonitrile in ether solution was added to the solution containing the Grignard reagent at a rate sufficient to maintain refluxing of the ether. The product was hydrolyzed with ammonium chloride solution and ether removed by distillation on the steam bath. The product was recovered by distillation at reduced pressure, boiling at about one hundred ninety degrees at a pressure of twenty mm. of mercury. This product was recrystallized from methanol, forming white needles melting at fifty-three to fifty-four degrees. The substance was identified by its mixed melting point with an authentic sample of phenyl *p*-tolyl ketone. The yield of recrystallized substance was thirty-three per cent of the theoretical, based on the *p*-bromotoluene.

Picric acid was the solute chosen for this part of the work. The work of Landee has established the fact that the stronger acids are less prone to associate. Picric acid is a moderately strong electrolyte, and it was hoped by its use to minimize the association of the solute as much as possible. The picric acid used (Baker and Adams) was purified by recrystallization from ethanol and dried by filtration at the pump. Since the original contained no significant impurities except water, no further tests for purity were made.

Determination of Apparent Molecular Weights

In taking the melting points of the solutions at various concentrations, it was found that the melting points would drop slowly for a few determinations and then reach a constant value. This was attributed to ionization of the solute, the equilibrium apparently not being established at once in any of the solvents. When the melting points reached a constant value it was assumed that equilibrium had been reached.

The same general procedure was followed in taking the freezing points of the solutions of picric acid as that used in determining the cryoscopic constants of these solvents. The first run was made on benzophenone. The results indicated that picric acid was completely ionized in this solvent up to concentrations of about one one-hundredth molal. It was thereafter the practice, where consistent melting points could not be obtained for the pure solvent, to add a minute amount of picric acid to stabilize the melting point. It was then assumed that this amount was completely ionized, and on this basis the theoretical temperature drop was calculated. The melting point of the solvent was determined from the calculated freezing point depression.

The apparent molecular weights were calculated by means of the usual equation,

$$m = \frac{1000 \cdot g \cdot K_f}{\Delta T_f \cdot G}, \qquad (2)$$

all terms having the same significance as in equation (1).

The calculations of the degree of dissociation, from the apparent molecular weights, were made using the following equation:

$$\alpha = \frac{m_1 - m_2}{m_2(n-1)} \qquad (3)$$

where:

α = degree of dissociation

m_2 = apparent molecular weight

m_1 = molecular weight as calculated from formula

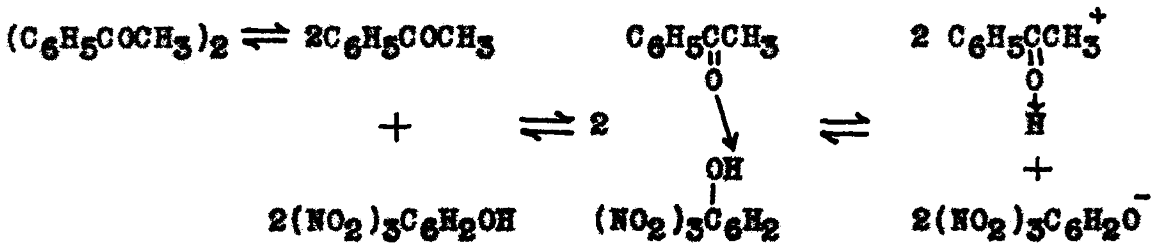
n = number of ions into which one molecule dissociates.

It must be admitted that this method is by no means ideal. There will always be a certain amount of association of the solute, increasing its apparent molecular weight, along with the dissociation which decreases its apparent molecular weight. What is actually measured is not either one of these factors, but the difference between them. That association does occur is easily seen by reference to the data obtained for solutions of picric acid in benzophenone. At the highest concentration the molecular weight is above the theoretical, a fact explained only by association of the solute. As stated above, both the solute and the solvents were so chosen as to minimize the effect of association, and it is the writer's belief that in the concentration range employed the association was not large. Nonetheless, the fact that a certain amount of association probably does occur must be taken into account in any interpretation of the results.

Effect of Solvent Association on Rate of Ionization

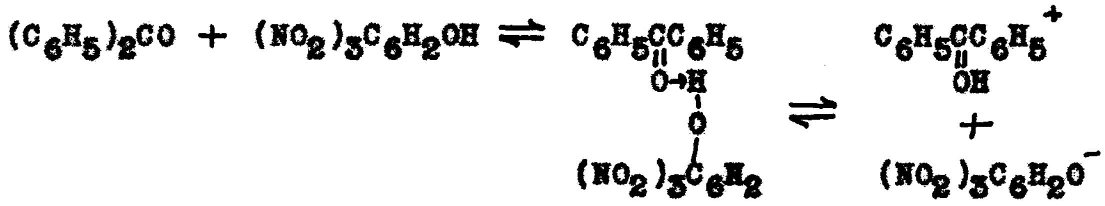
It is interesting to note the differences in time required for the solutions to attain equilibrium. From considerations of steric effect alone, one might expect the dissociation to reach equilibrium much more rapidly in acetophenone than in benzophenone. Actually the reverse is true. Solutions in benzophenone reached final equilibrium in about thirty minutes in all cases, while solutions in acetophenone often required as much as two days for final equilibrium to be established. Propiophenone behaves much like acetophenone in this respect, while phenyl p-tolyl ketone resembles benzophenone. The author believes this due to the fact that the acetophenone and propiophenone possess "active" methylene groups, active in the sense that the hydrogen of these groups is replaceable with metal. Compounds possessing replaceable hydrogen atoms are the most prone to association by the formation of hydrogen bridges, as witness the organic acids, alcohols, phenols, amides, etc.

If association of this type does occur in acetophenone and propiophenone, then we have present an equilibrium which is at least as complicated as the following:



$$(C_6H_5COCH_3)_2 \rightleftharpoons 2C_6H_5COCH_3 + 2(NO_2)_3C_6H_2OH \rightleftharpoons 2\,\overset{C_6H_5\overset{\displaystyle C}{}CH_3}{\underset{(NO_2)_3C_6H_2}{\underset{|}{\underset{OH}{\underset{\searrow}{O}}}}} \rightleftharpoons 2\,\overset{C_6H_5CCH_3^{+}}{\underset{2(NO_2)_3C_6H_2O^{-}}{\underset{+}{\underset{\overset{+}{H}}{O}}}}$$

On the other hand, in the cases of benzophenone and similar compounds, no "active" methylene groups are present and association of this type would not occur. In this case the equilibrium involved would be much simpler.



$$(C_6H_5)_2CO + (NO_2)_3C_6H_2OH \rightleftharpoons \overset{C_6H_5CC_6H_5}{\underset{(NO_2)_3C_6H_2}{\underset{|}{\underset{O}{\underset{|}{O\rightarrow H}}}}} \rightleftharpoons \overset{C_6H_5CC_6H_5^{+}}{\underset{(NO_2)_3C_6H_2O^{-}}{\underset{+}{OH}}}$$

In the first type of system, if the rate of dissociation of the double molecules into single molecules was comparatively slow, this might easily be the controlling rate, and thus it would determine the speed with which final equilibrium was established. In such a case it is easily conceivable that the steric factors involved might be negligible in comparison and the apparent discrepancy accounted for.

Presentation of Data

The data for ionization in those solvents for which results could be obtained are tabulated on the following pages. Table 3 shows the ionization of picric acid in propiophenone; Table 4, in acetophenone; Table 5, in phenyl p-tolyl ketone; and Table 6, in benzophenone. In all cases, the concentration range employed is from zero to one-tenth molal. The sequence of the tables is in the order of decreasing dissociation.

These data are also presented in graphical form. In Figure 2 the ionization of picric acid (as calculated from the apparent molecular weights by equation [3]) is plotted as a function of concentration for each of the various solvents employed. Above a concentration of five-hundredths molal, where all freezing point depressions were at least one-half degree, these curves parallel each other fairly well. The order of decreasing dissociation in these solvents is propiophenone $>$ acetophenone $>$ phenyl p-tolyl ketone $>$ benzophenone. This is also in the order of increasing positive electron-sharing ability of the radical R attached to the carbonyl group.

In order to show more clearly the relationship between the electron-sharing abilities of the R groups and the ionizing power of these solvents, in Figure 3 are plotted the ionizations of picric acid in each of these solvents,

TABLE 3

Apparent Molecular Weight of Picric Acid in Propiophenone

Molality of picric acid	Melting point	ΔTf	Kf	Apparent mol. wt.	Per cent ionized
0.00	15.43**	---	----	-----	-----
0.00525	15.37	.06**	5.55	114.5*	100*
0.0316	15.08	.35	5.55	114	100
0.0543	14.85	.58	5.55	119	92.5
0.0780	14.63	.80	5.55	123	85.5
0.0977	14.47	.96	5.55	129	77.5

*Assumed value.
**Calculated from assumed value.

TABLE 4

Apparent Molecular Weight of Picric Acid in Acetophenone

Molality of picric acid	Melting point	ΔTf	Kf	Apparent mol. wt.	Per cent ionized
0.00	19.35	---	----	-----	-----
0.009	19.25	.10	5.65	113	100
0.0223	19.10	.25	5.65	114	100
0.0360	18.91	.44	5.65	110	100
0.0570	18.80	.55	5.65	120	91
0.0655	18.68	.67	5.65	126	82
0.0790	18.54	.81	5.65	126	82
0.0932	18.43	.92	5.65	131	75
0.106	18.33	1.02	5.65	134	71

TABLE 5

Apparent Molecular Weight of Picric Acid in Phenyl p-tolyl Ketone (m.p., 51.75°C.)

Molality of picric acid	Melting point	ΔTf	Kf	Apparent mol. wt.	Per cent ionized
0.0072	51.61	.14**	9.58	114.5*	100*
0.0155	51.47	.28	9.58	121	90
0.0327	51.26	.48	9.58	150	52.5
0.0525	51.10	.65	9.58	178	28.6
0.0743	50.85	.90	9.58	182	25.8
0.0955	50.57	1.18	9.58	178	28.6

*Assumed value.
**Calculated from assumed value.

TABLE 6

Apparent Molecular Weight of Picric Acid in Benzophenone

Molality of picric acid	Melting point	ΔTf	Kf	Apparent mol. wt.	Per cent ionized
0.00	47.67	---	----	-----	-----
0.0085	47.50	.17	9.87	113	100
0.0168	47.35	.32	9.87	118.6	93
0.0264	47.23	.44	9.87	136	69
0.0334	47.19	.48	9.87	157.5	45.5
0.0415	47.13	.54	9.87	174	32
0.0525	47.04	.63	9.87	189	21
0.0702	46.90	.77	9.87	206	11
0.0890	46.73	.94	9.87	214	7
0.133	46.40	1.27	9.87	236	(3)

as a function of the electron-sharing abilities of the radicals. Curves are drawn for the concentrations five-hundredths, six-hundredths, seven-hundredths and nine-hundredths molal. The degree of significance which may be attached to the form of these curves will be considered in the discussion of the results.

DISCUSSION OF RESULTS

Relationship between Ionizing Power of Solvents and Electron-sharing Abilities of Substituent Groups

The results follow, at least in a qualitative way, the predictions made in the theoretical portion of this thesis. Those solvents in which R has a large electron-sharing ability possess less ionizing power than those in which the electron-sharing ability of R is small. This relationship is shown graphically in Figure 3.

Effect of Dielectric Constant of Solvent

Unfortunately, data on the dielectric constants of these compounds were available only for acetophenone, benzophenone and propiophenone. Such data as were available are tabulated, in part, in Table 2. The values of the dielectric constants reported are those given for the temperatures nearest the temperatures at which the runs were made.

These data indicate that the dielectric constants of these solvents were of secondary importance in determining their ionizing powers. Whereas propiophenone has a smaller dielectric constant than does acetophenone, the former

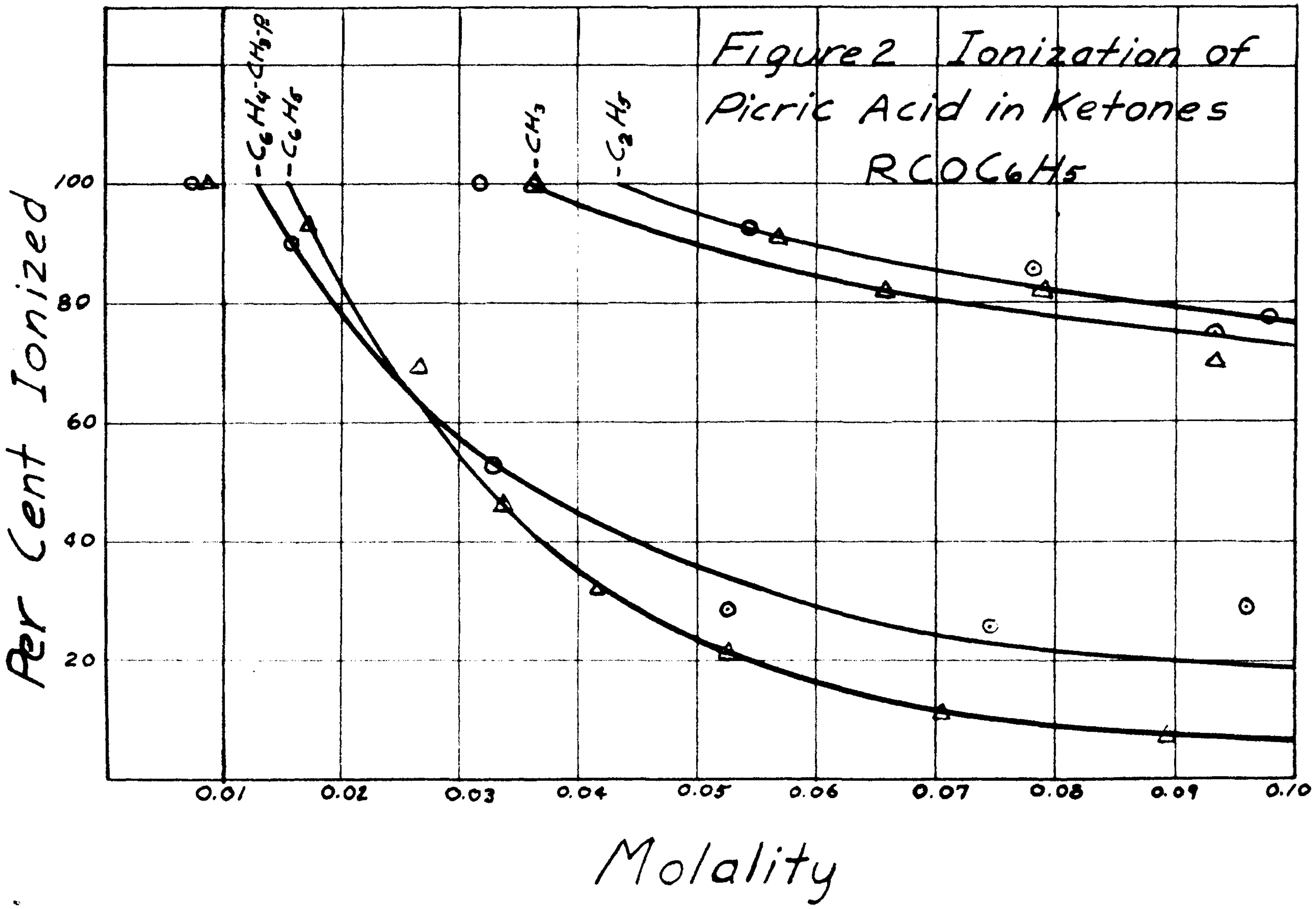


Figure 2 Ionization of Picric Acid in Ketones $RCOC_6H_5$

solvent proved to have slightly greater ionizing power. Of greater significance is the fact that, while the variation of the dielectric constants of these solvents is small and fairly regular, the variations in their ionizing powers are neither small nor regular. Both acetophenone and propiophenone possess far greater ionizing power than does benzophenone. In order to show the relationship between the ionizing power and the dielectric constant of each of these solvents, the dielectric constants are also plotted (dotted line) in Figure 3 as a function of the electron-sharing abilities of R.

Effect of Temperature Variations

It is unfortunate that, since the ionization constants for all electrolytes vary with changes in the temperature, all of these determinations could not have been run at the same temperature. This is obviously impossible for determinations made by the cryoscopic method. However, the possibility that the differences in ionization are due to temperature differences in the determinations is precluded by the fact that the effect is not a regular one. Reference to Table 2 will establish the fact that phenyl p-tolyl ketone would be out of order if this were the case. While it has the highest melting point of any of the substances investigated, it occupies an intermediate position in

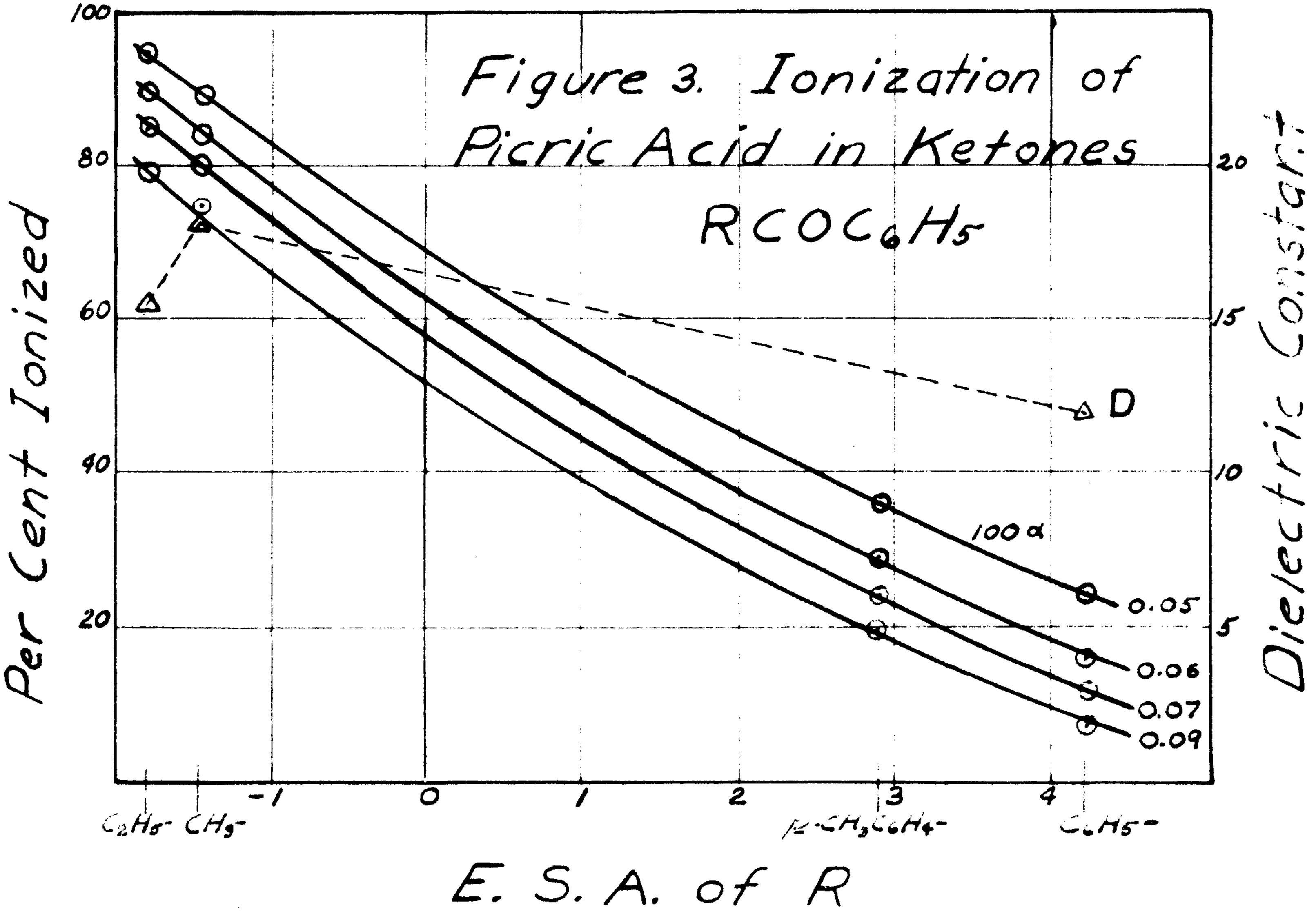


Figure 3. Ionization of Picric Acid in Ketones $RCOC_6H_5$

ionizing power. Further, since the heat of ionization of a weak acid is generally quite small, at least in aqueous solution, it is the opinion of the author that this effect is not large.

Nevertheless, although the variant temperature effects are unlikely to be large enough to reverse the order of ionizing power, they are quite likely to be large enough to affect the shape of the curves shown in Figure 3. Both solvents which showed the higher degree of ionizing power melted at temperatures around twenty degrees, the other pair of solvents at about fifty degrees. If heat is absorbed in the ionization process, then the results for acetophenone and propiophenone (low temperature) are probably relatively too low as compared to what they would be at the higher temperature. On the other hand, if heat is evolved in the ionization process, then the results for benzophenone and phenyl p-tolyl ketone are low, relative to their values at about twenty degrees. In either case it would appear that one pair of results is relatively too low, and it is likely that the curves in Figure 3 should show more of a curvature. In any case, it is extremely doubtful if the shape of the curves, as drawn in Figure 3, can be assigned any significance.

Proper Choice of Units of Concentration

Before leaving this discussion, one more factor should be taken into account. The choice of molality as a unit of concentration leaves much to be desired. If the ionizing power of a solvent is dependent, under certain conditions, upon its ability to solvate the acid and carry away the solvated proton, then a fairer comparison would be made on a basis of equal numbers of moles of solvent, rather than an equal number of grams of solvent. For example, in one thousand grams of acetophenone there are present more molecules, and thus more functional groups to solvate the proton than are present in an equal weight of propiophenone. While the results show propiophenone to have slightly more ionizing power than acetophenone, the actual difference is somewhat greater since there were less molecules present in the propiophenone solution. The same considerations apply equally to phenyl *p*-tolyl ketone and benzophenone.

In Figure 4 are plotted the ionizations of picric acid in each of the solvents as a function of the mole fraction of acid in each solvent. Reference to this figure will establish the fact that the difference in ionizing power of these solvents is somewhat greater than that indicated in Figure 2, as is apparent from the above considerations.

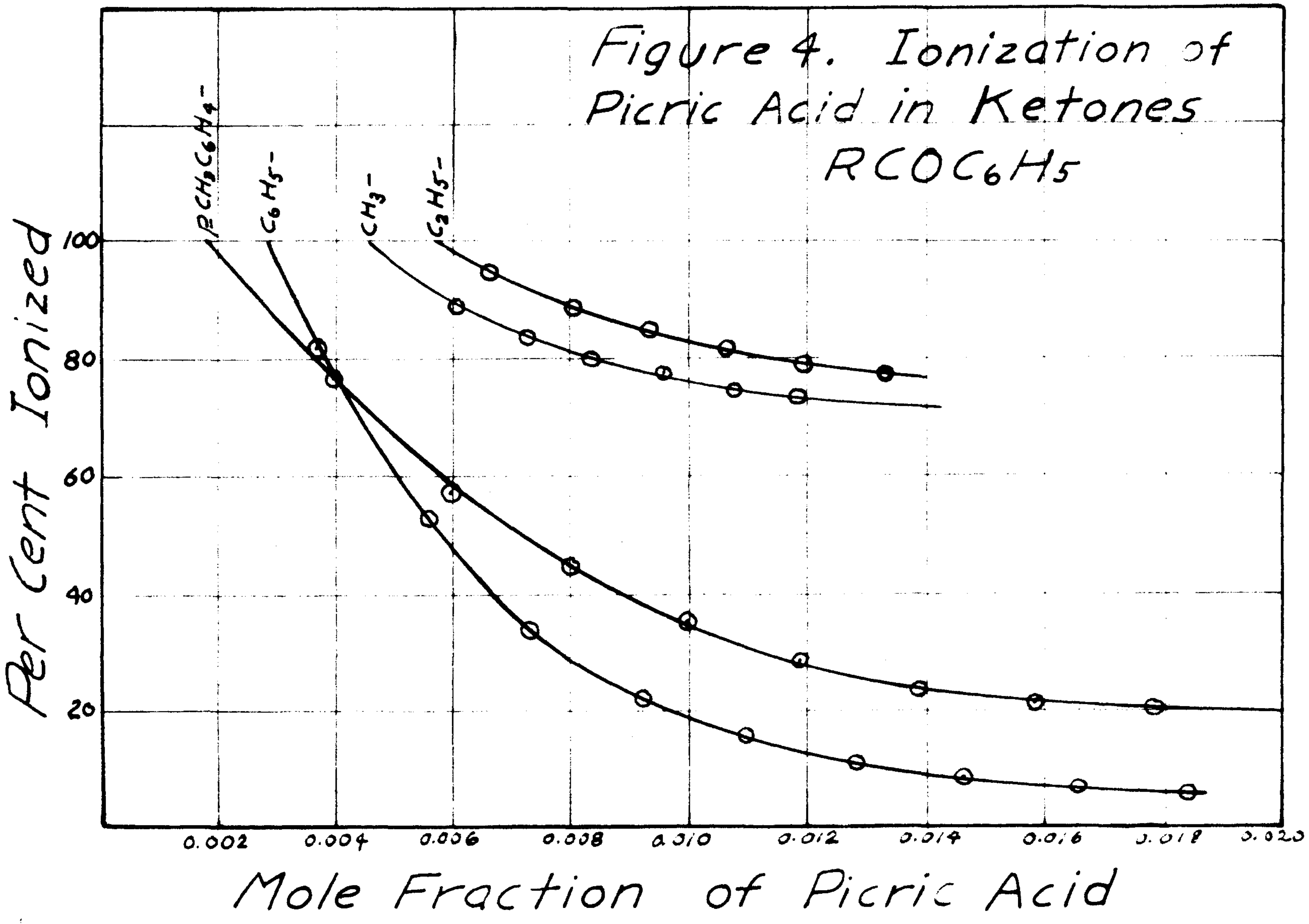


Figure 4. Ionization of Picric Acid in Ketones $RCOC_6H_5$

While it is apparent from the foregoing discussion that the results obtained in this portion of the work cannot be taken as absolute values, it is the contention of the author that the results bear out, at least qualitatively, the postulates stated in the theoretical portion of this thesis concerning the relationship between the ionizing power of a solvent and the electronic properties of radicals attached to the functional group of the solvent molecule. However, it is an obvious fact that the cryoscopic method is not a very desirable one for making measurements of this type as it is subject to errors due to temperature differences, small freezing point depressions at low concentrations, exposure to impurities in the air, etc. Therefore, the second portion of the experimental work was done using the conductance method, a standard method long used in the measurement of ionization in both aqueous and non-aqueous solutions.

PART II. CONDUCTIMETRIC MEASUREMENTS

EXPERIMENTAL

Apparatus

This part of the work was undertaken, not only to measure the ionization by a method independent of that used in the previous part of the work, but also because of the extremely limited applicability of the cryoscopic method to problems involving the use of different solvents, and because of the many disadvantages inherent in the cryoscopic method, such as the large experimental errors at low concentrations and the impossibility of making all measurements at the same temperature.

A great deal of work has been done in the field of electrolytic conduction on both aqueous and non-aqueous solutions. However, as stated in the theoretical discussion, most of the work concerning non-aqueous solutions has been done in a relatively few solvents and nearly all of it in the field of strong electrolytes. Hence there are no data sufficiently comprehensive to be applicable to the problem at hand under the conditions laid down in the theoretical part of this discussion.

The conductance apparatus, its sources of error and proper design have been the subject of a good many investigations. A summary of the earlier work in this field and of its development from an historical standpoint has been made by Morgan and Lammert (51). A brief summary of the findings to date, the requirements of apparatus for obtaining various degrees of accuracy, and a bibliography of leading references to the literature on the subject of conductance measurement were presented in a recent catalog of the Leeds and Northrup Co. (42).

The accepted standard for high-precision measurements is the design of Jones and Josephs (34). The apparatus used in this study employs the circuit recommended by them although no attempt was made to employ all the refinements suggested by these investigators. This was believed unnecessary as the present study was concerned primarily with the conductance ratio and not with the absolute conductance. The wiring diagram for the apparatus used is shown in Figure 5.

The oscillator used was a vacuum tube type, built for this laboratory by the Gulliver Radio Co. of this city, based on a design by Kelley (35). This unit operated from the hundred ten volt a.c. line and gave an output current of good sinusoidal form at a frequency of one thousand cycles per second. The output voltage was kept the same

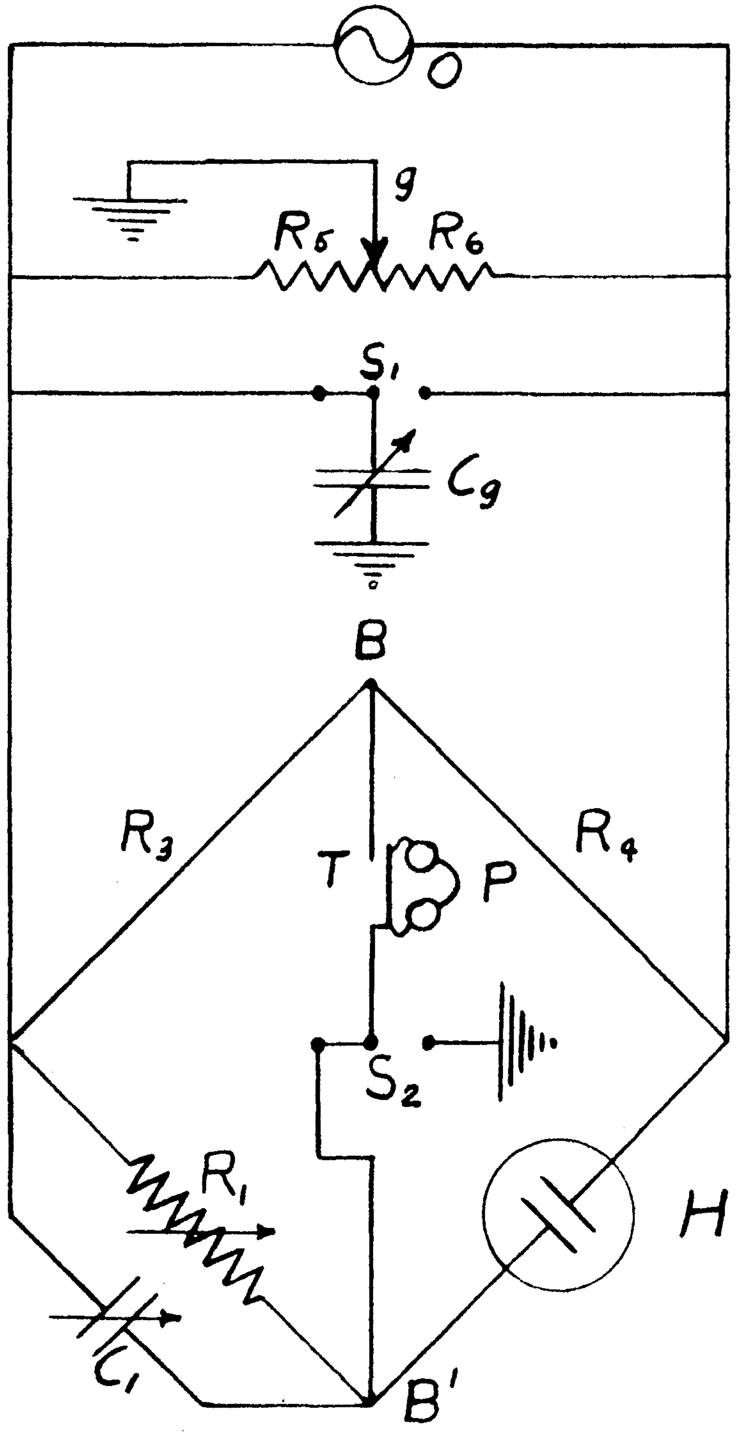


Figure 5. Apparatus for Conductance Measurements

in all the measurements, at about six volts.

The resistances R_3 and R_4 were furnished by a Leeds and Northrup student-type slide wire. The resistances R_5 and R_6 in the grounding circuit must be variable if R_3 and R_4 are variable, and for this purpose a second slide wire of the same type was used.

The standard resistances used, R_1, were probably the largest sources of error in the apparatus. One of these was a decade type, manufactured by Leeds and Northrup, reading from one to ten thousand ohms in steps of one ohm. The other was a student's standard high resistance, reading from ten thousand to one hundred thousand ohms in steps of ten thousand ohms. Both of these units were designed primarily for use with direct current and are not particularly accurate when used with alternating current. However, it was established that while these resistances might not be accurate when used with alternating current they were at least fairly consistent, that is, one of these resistances could be used to measure the other. The maximum error for such a measurement did not exceed two per cent in terms of the values indicated on the apparatus. Thus while the absolute values determined for the conductances would be in error, these errors should enter into the values for the limiting conductances in about the same proportion, so that the conductance ratios and the ionization constants determined therefrom should be accurate enough for the purpose at hand.

The coils for these resistances were bifilar wound, eliminating inductance errors, but they were not so wound as to eliminate capacitance. Capacitance was particularly large in the high resistance box, and when this resistance was used it was found necessary to shunt an auxiliary capacitance of one thousand micro-micro-farads (not shown in Figure 4) across the cell. This condenser, used in conjunction with the variable condenser C_1, insured good sound minima at all resistances encountered.

The condenser C_1, used to compensate capacitance in the cell, was a variable air condenser manufactured by the General Radio Co., having a capacitance variable between forty-eight and one thousand thirty-four micro-micro-farads. The condenser C_g in the grounding circuit was a small unit manufactured by the Allied Radio Corp., having a maximum capacitance of about one hundred and fifty micro-micro-farads.

The cells used were of the usual student type. A drawing of one of these is shown in Figure 6. The electrodes were fairly large (about sixty sq. mm.) and set quite close together (about seven mm.). The cell constants were determined in the usual way, using one-hundredth normal potassium chloride as reference solution, and were of the order of eighteen-hundredths reciprocal centimeter. These are approximately the figures for the cells designed by Washburn (72) and approved by Morgan and Lammert (49) for solutions of moderate conductance, and they were considered good enough for the order of accuracy to be attained. They proved quite satisfactory, having a particularly low capacitance for most of the solutions encountered.

The telephones for detecting the balance point were of the usual radio-headphone type. They were connected across the tap key T so that the circuit might be broken readily, this being a considerable aid in the detection of very faint sounds in the telephones.

The grounding circuit shown is the modified Wagner ground recommended by Jones and Josephs. A considerable capacitance always exists between the telephone coils and the observer, and it is the function of the grounding circuit to keep from charging current into this capacitance by maintaining both the coils and the observer at ground potential. In view of the other errors inherent in the equipment used, the error due to this effect was probably negligible, but use of the grounding circuit had the effect of sharpening the minimum point and hence was a convenience to the operator whether or not it was an unnecessary refinement. Further, the oscillator was of a type requiring

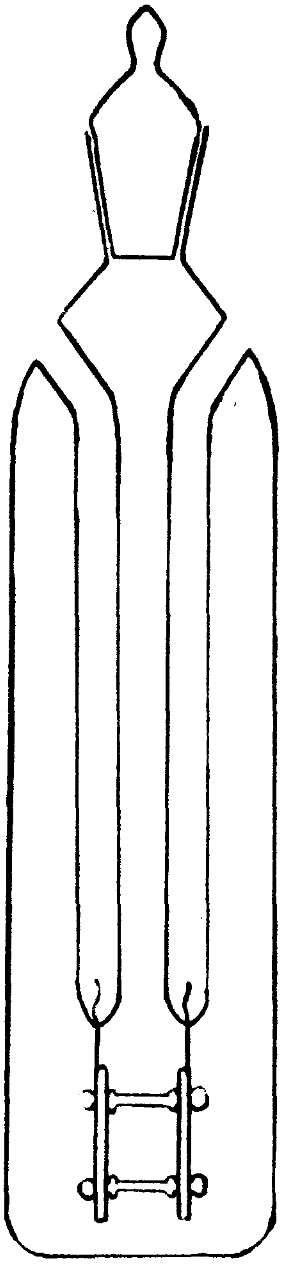


Figure 6. The Cell

grounding of one of the output terminals, and the grounding circuit served to do this.

The procedure used in adjusting the bridge was as follows:

(1) Balance bridge by adjusting R_1 and C_1.

(2) By means of switch S_2, disconnect telephone from B' and connect it to ground.

(3) Adjust g and C_g across R_5 and R_6 until no sound is heard in the telephone. B is now at ground potential.

(4) By means of switch S_2, disconnect telephone from ground and connect it to B'.

(5) Make final adjustment of bridge with R_1 and C_1. If this differs much from the first setting, repeat the process.

Temperature control was achieved by means of a small thermostat designed by Dr. Johns of this laboratory. The circuit for this unit is shown in Figure 7 and is a modification of one suggested by Dr. L. D. Goodhue of the U. S. Dept. of Agriculture (22). The bath itself was an aluminum block with an external diameter of six inches. Holes bored from the bottom of the block served as inlets for the cooling water and as wells for the heating coils. Holes were drilled in the top of the block for a thermometer and for a mercury thermoregulator. The RCA 1904 tube shown serves

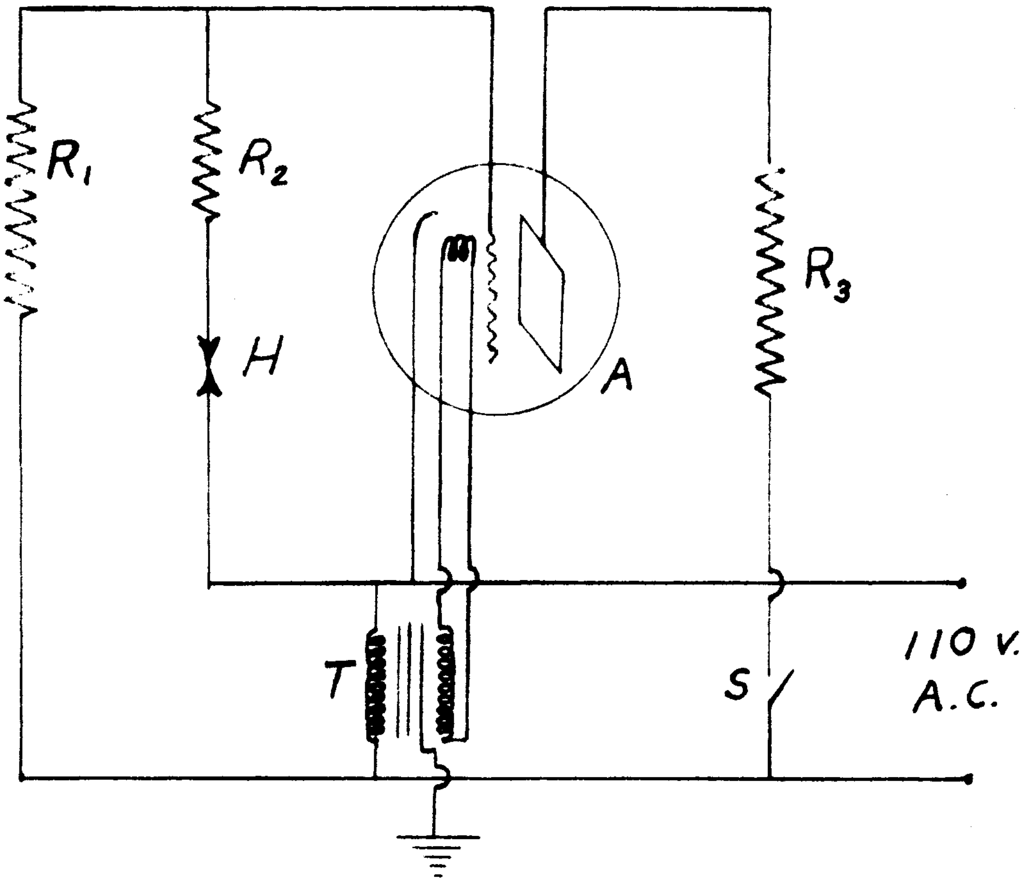


Figure 7. Electrical Circuit for Thermostat

R_1 - 50,000 ohm, 1 watt radio resistor.

R_2 - 1500 ohm, 1 watt radio resistor.

R_3 - Bath heater, 130 ohms.

H - Mercury thermoregulator.

A - R.C.A. 1904 vacuum tube.

T - Transformer. 110 v. primary; 5 volt, 5 amp. secondary.

S - Toggle switch.

both as a relay and as a source of current for the heating coils.

Shielding of the apparatus was tried at first, but in view of the accuracy desired it was not really necessary, and the copper screen used as the shielding material worked through the insulation of the wires passing through it and caused troublesome short circuits. This practice was finally discontinued.

Technique

The procedure followed in cleaning the cells was as follows. Before a run the cell was filled with cleaning solution and let stand overnight. It was then washed out thoroughly with distilled water, followed by several washings in acetone which had been previously distilled to preclude the possibility of any solid material being present. Following this, the cell was dried in a current of purified nitrogen and filled at once with the solution to be measured. For any given set of solutions, washing between determinations made on the individual members of the set was with the redistilled acetone only, followed by drying in the usual manner.

The electrodes were not platinized in making these determinations. While platinization of the electrodes is certainly an advantage in overcoming polarization, it has certain disadvantages which prohibit its use with non-aqueous solutions. It has been shown (58) that the catalytic effects of the platinum may cause chemical changes in the solvent. For example, alcohols are easily oxidized in this way. These catalytic effects will obviously be much greater with platinum black than with bright platinum. The platinum black also has much greater adsorptive power than does bright platinum, and this makes difficult the cleaning of the cell between determinations on the individual members of a set of solutions.

In view of the time required for equilibrium to be established, as shown by the previous experimental part of this study, it was thought best not to make any dilutions in the cell itself. Consequently, the solutions were made up in small Erlenmeyer flasks. These flasks were cleaned, dried and filled with purified nitrogen in exactly the same way as that used for the conductance cell. In all cases the solution of highest concentration was made up first, and the other solutions of lower concentrations were made up by successive one to one dilutions. After the solutions had been made up, they were allowed to stand for a time sufficient to insure that equilibrium had been established.

Transfer of the solutions from flask to cell was accomplished by means of a dry pipet filled with purified nitrogen. As both flask and cell were filled with nitrogen before the transfer, this procedure eliminated all contact with the air. This is quite necessary, as it was found that merely pouring the solution from flask to cell allowed enough contact with the air to make the results run considerably too high at the lower concentrations. This is likely due to the absorption of small amounts of water from the atmosphere.

After the filled cell had been placed in the thermostat, about one-half hour (or less, depending on the difference between room temperature and bath temperature) was allowed for the solution to come to the temperature of the bath before taking the first reading. A second reading was taken ten minutes later. If the values checked, it was assumed that temperature equilibrium had been reached; if not, a third reading was taken ten minutes later, and so on until two consistent readings were taken on successive attempts.

Purification of Materials

As solvents, a series of ketones of the type CH_3COR was chosen first since previous work had shown the lower members of this series to have a fair degree of ionizing power. Also, it was possible to choose a representative series of these compounds so that there was little difference between the dielectric constants of the individual members. The solvents chosen were acetone, methyl ethyl ketone and acetophenone. Pertinent physical data on these compounds are presented in Table 7. It should be stressed again that the values obtained by the author for the conductances of these compounds are not to be regarded as being highly accurate. Conductances of the pure solvents were determined for use in correcting the conductances of their solutions and as an approximate check on the purity of the compounds, and not with the intention of determining new and more accurate values for the conductances as such.

Acetone for the conductance measurements was prepared by fractionating stock acetone seven times. Its boiling point was fifty-five and two-tenths degrees at a pressure of seven hundred forty mm.

Methyl ethyl ketone (Eastman) was fractionated seven times, boiling at seventy-eight degrees at a pressure of seven hundred forty mm.

Acetophenone (Eastman) was purified by distillation under reduced pressure in an atmosphere of purified nitrogen. Its boiling point was ninety-one degrees at a pressure of fourteen mm.

The purities of all of these compounds were judged by their conductances, which are reported in Table 7.

It was desired to determine the ionization constants of the acid in a second series of solvents in order to see whether or not the relationships preducted in the theoretical part of this thesis were independent of the type of solvent employed. A series of nitriles of the type RCN was selected, including acetonitrile, benzonitrile, phenylacetonitrile and propionitrile. Pertinent physical data on these compounds are presented in Table 8.

Acetonitrile (Eastman) was fractionated at atmospheric pressure a sufficient number of times to obtain a desirable conductance. It boiled at a temperature of eighty-one degrees at a pressure of seven hundred forty mm.

Propionitrile (Eastman) was purified in the same way, except that it was allowed to stand over anhydrous sodium sulfate for three days prior to fractionation. It boiled at a temperature of ninety-six degrees at a pressure of seven hundred forty mm.

Benzonitrile (Eastman) was purified by distillation at reduced pressure in an atmosphere of purified nitrogen. (Boiling point: eighty-five degrees at seventeen mm. pressure).

Phenylacetonitrile (Eastman) was purified in the same way as the benzonitrile. (Boiling point: one hundred seventeen degrees at twenty-two mm. pressure).

The purities of all of these nitriles were judged by their conductances, which are reported in Table 8.

TABLE 7

Physical Constants of Ketones $RCOCH_3$

Substance	Dielectric constant	Specific conductance at 25°C. Author's value	Comparative value
Acetone	20.7 at 17° 21.5 at 20°	1.46x10^{-7}	1.73x10^{-7}(62) ~~0.60~~x10^{-7}(37) 0.58
Acetophenone	18.1 at 20°	0.97x10^{-7}	1.80x10^{-7}(62) ~~0.06x10^{-7}(50)~~ 0.55x10^{-7} (37)
Methyl ethyl ketone	17.8 at 20°	1.65x10^{-7}	1.00x10^{-7}(62) 1.00x10^{-7}(13)

TABLE 8

Physical Constants of Nitriles RCN

Substance	Dielectric constant	Specific conductance at 25°C. Author's value	Comparative value
Acetonitrile	38.8 at 20°	5.3x10^{-7}	3.8x10^{-7}(62)
Benzonitrile	26.5 at 20°	0.66x10^{-7}	0.80x10^{-7}(62)
Phenylacetonitrile	18.4 at 20°	1.10x10^{-7}	0.50x10^{-7}(62)
Propionitrile	27.0 at 20°	3.00x10^{-7}	10x10^{-7}(62)

Picric acid proved to be the best solute for use with these solvents, giving solutions of sufficiently high conductance to keep the experimental error within bounds. It was purified by the same method as that described in Part I. 3,5-Dinitrobenzoic acid was also tried as solute, but the conductances of its solutions were small and the results not sufficiently accurate.

Conductance Data and Ionization Constants of Picric Acid in Ketones

The conductances of picric acid in these solutions were measured at twenty-five degrees. The data obtained are tabulated in Tables 9, 10, and 11 and presented graphically in Figure 8.

Two methods were used in the extrapolation of the equivalent conductance to its value at infinite dilution, one serving as a check on the other. Both methods are based on the same assumption, namely that the law of mass action is followed, in its simple form, over at least a part of the concentration range. Taking as an example the following simple dissociation,

$$HA \rightleftharpoons H^+ + A^- ,$$

let the concentration be C and the degree of dissociation be α. Then, if the law of mass action holds, the value of

TABLE 9

Conductance of Picric Acid in Methyl Ethyl Ketone at 25°C.

Concentration	Specific conductance	Dilution (cc.)	Equivalent conductance
0.10	82.9×10^{-7}	1×10^4	0.0829
0.05	62.9×10^{-7}	2×10^4	0.1259
0.025	41.5×10^{-7}	4×10^4	0.1662
0.0125	28.7×10^{-7}	8×10^4	0.2300
0.00625	19.7×10^{-7}	16×10^4	0.3150
0.00312	13.5×10^{-7}	32×10^4	0.4325

$\Lambda_0 = 1.95$
$K = 1.98 \times 10^{-4}$

TABLE 10

Conductance of Picric Acid in Acetone at 25°C.

Concentration	Specific conductance	Dilution (cc.)	Equivalent conductance
0.10	252.5×10^{-7}	1×10^4	0.2525
0.05	193.8×10^{-7}	2×10^4	0.388
0.025	136.8×10^{-7}	4×10^4	0.547
0.0125	93.0×10^{-7}	8×10^4	0.740
0.00625	66.7×10^{-7}	16×10^4	1.040
0.00312	48.5×10^{-7}	32×10^4	1.400
0.00156	30.2×10^{-7}	64×10^4	1.925

$\Lambda_0 = 7.5$
$K = 1.38 \times 10^{-4}$

TABLE 11

Conductance of Picric Acid in Acetophenone at 25°C.

Concentration	Specific conductance	Dilution (cc.)	Equivalent conductance
0.10	3.94×10^{-7}	1×10^{4}	0.00394
0.05	2.49×10^{-7}	2×10^{4}	0.00498
0.025	1.65×10^{-7}	4×10^{4}	0.00660
0.0125	1.24×10^{-7}	8×10^{4}	0.00995
0.00625	1.09×10^{-7}	16×10^{4}	0.01744
0.00312	0.35×10^{-7}	32×10^{4}	0.01120

$\Lambda_0 = 0.33$
$K = 1.5\times10^{-5}$

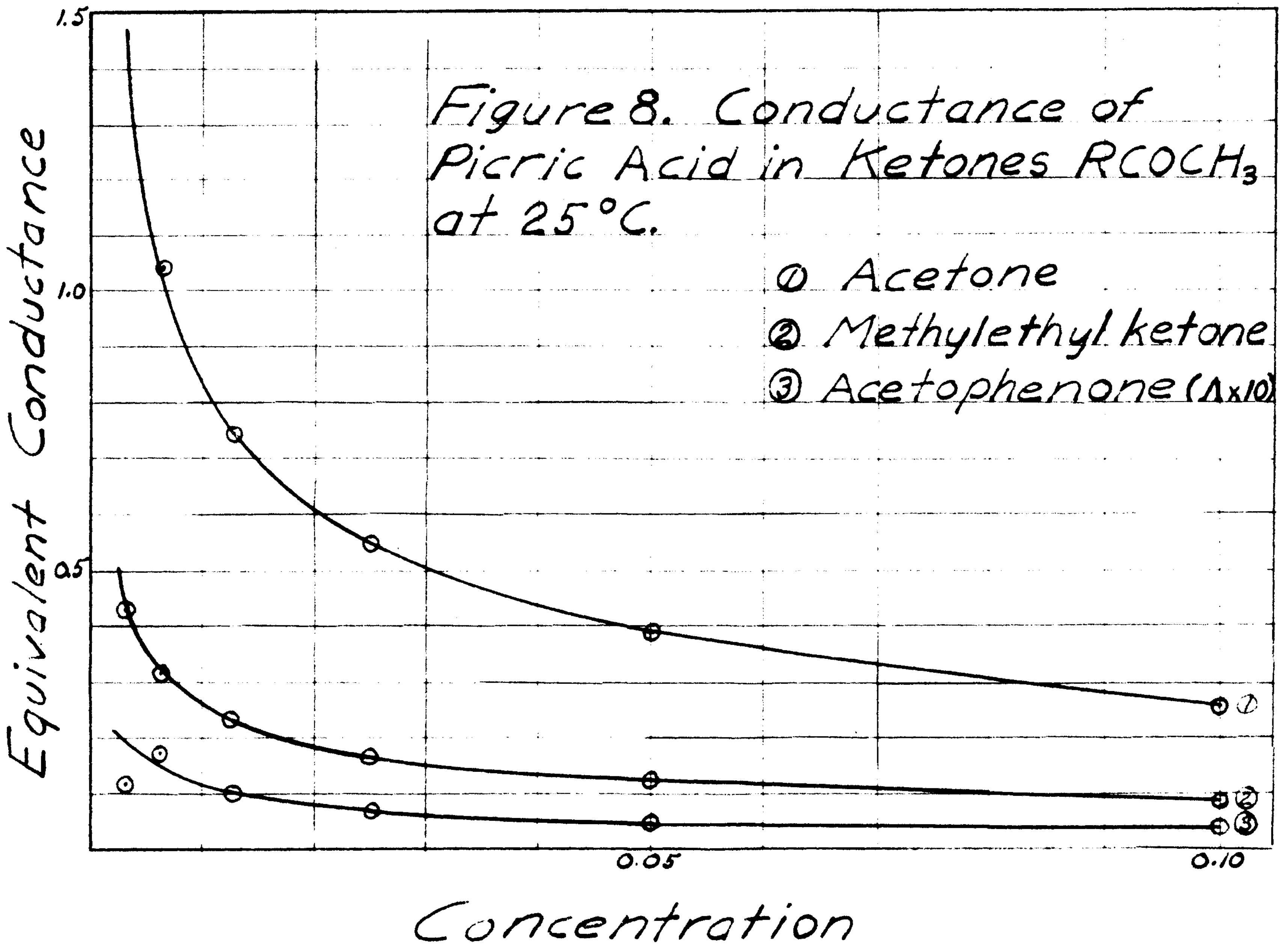


Figure 8. Conductance of Picric Acid in Ketones $RCOCH_3$ at 25°C.

the equilibrium constant will be given by the expression,

$$(4) \qquad K = \frac{(C\alpha)^2}{(1-\alpha)C} = \frac{C\alpha^2}{1-\alpha}.$$

Assuming that in the case of a weak acid the conductance ratio is equal to the degree of dissociation and substituting the conductance ratio for the degree of dissociation in equation (4) and rearranging, we obtain

$$(5) \qquad K = \frac{C\Lambda^2/\Lambda_o^2}{1-\Lambda/\Lambda_o} = \frac{C\Lambda^2}{\Lambda_o(\Lambda_o-\Lambda)}.$$

By rearrangement equation (5) may be written in the following form:

$$(6) \qquad C\Lambda = \frac{K\Lambda_o^2}{\Lambda} - K\Lambda_o = \frac{A}{\Lambda} - B$$

where A and B are constants.

Then, if our assumptions are justified, a plot of $C\Lambda$ (equal to the specific conductance times ten to the third power) against $1/\Lambda$ should be a straight line. Extrapolation of this line to the axis $C\Lambda$ equals zero gives the value of $1/\Lambda$ for an infinitely dilute solution, from which the value of Λ_o may be calculated. The assumption that the mass law would be followed over at least a part of the concentration range seemed a reasonable one, since the measurements were being made on an organic acid in solvents possessing much less ionizing power than does water. This was found, indeed, to be the case. Straight lines were obtained, within the limits of experimental error, for all solutions at the lower end of the concentration range. This method of extrapolation is illustrated in Figure 9 for the solution of picric acid in methyl ethyl ketone.

The chief disadvantage of this method lies in the difficulty of reading accurately the value of $1/\Lambda$ at its intercept when Λ_0 is very large. Therefore, the method of Washburn (73) was used as a check. This method is also based on equation (5). It consists of plotting K of equation (5) against the concentration, assuming values for Λ_0. In the region of concentration where the law of mass action is followed, K is independent of concentration. Therefore, if the value of Λ_0 has been assumed correctly, in this region the curve becomes a straight line approaching the K axis at right angles. If the value of Λ_0 is not correctly chosen, the curve is not perpendicular to the K axis, but slopes up or down. Since the value of Λ_0 is already known fairly accurately from the first extrapolation method, little trial and error in determining the value for Λ_0 is necessary. This method is somewhat more sensitive than the graphical method for solutions where Λ_0 is large. The method is illustrated in Figure 10 for the solution of picric acid in methyl ethyl ketone. This method gives at the same time the ionization constant for the acid in the solvent under consideration.

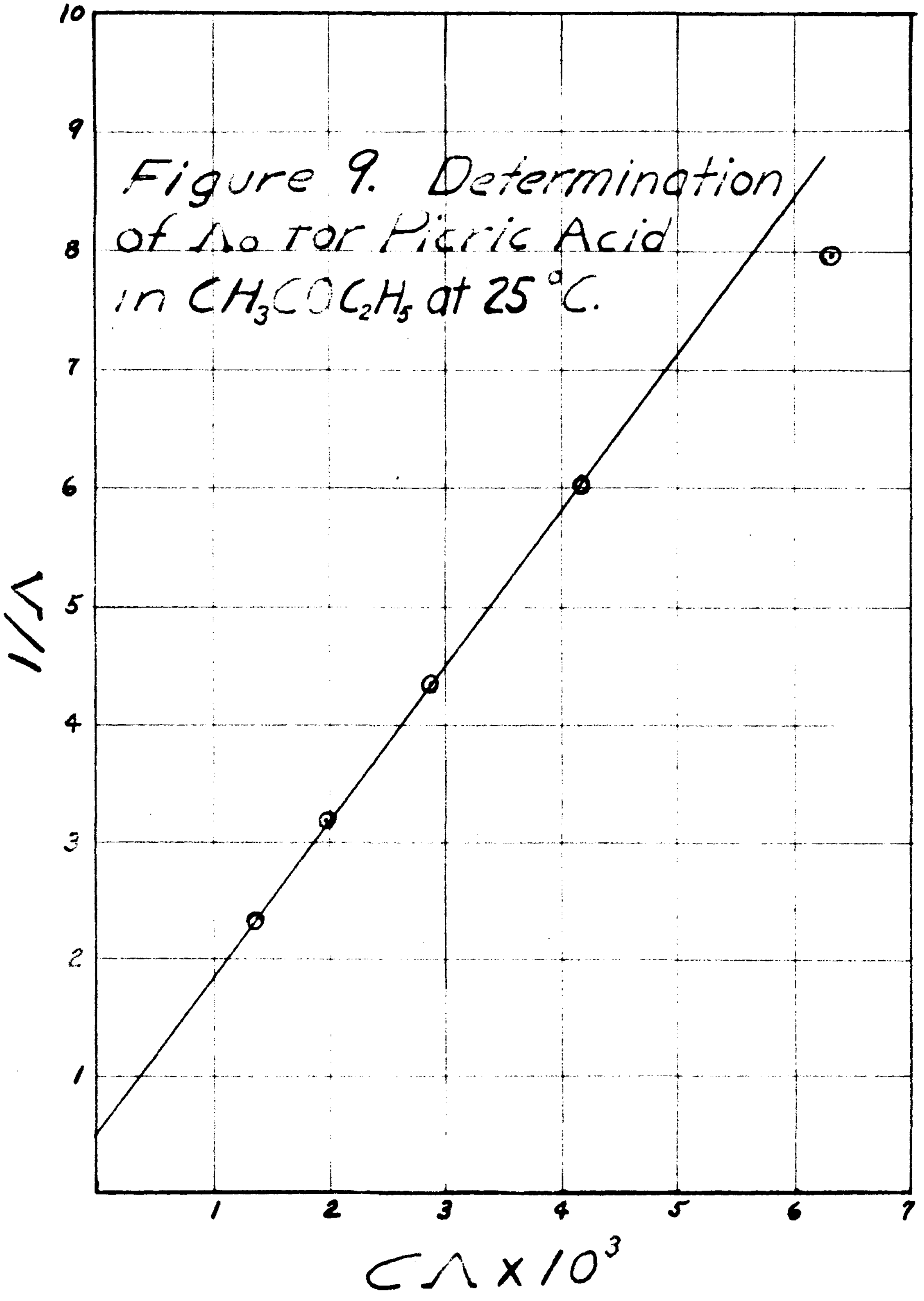


Figure 9. Determination of Λ_0 for Picric Acid in $CH_3COC_2H_5$ at 25 °C.

The equivalent conductances at infinite dilution, together with the ionization constants of picric acid in each of the solvents as determined by the methods outlined above, are given in Tables 9, 10, and 11, along with the conductance data for these solutions.

The results for picric acid in acetophenone were somewhat erratic due to the extremely low conductances in this solvent, and the ionization constant found for picric acid in this solvent is probably not of the same accuracy as the constants found for the acid in the other two solvents. However, in the author's opinion, there can be no question but that this solvent had less ionizing power than the other two. Solutions in the acetophenone were almost water-white at the lower concentrations. In the other two solvents at the same concentrations the solutions were distinctly yellow. The yellow color of picric acid solutions is very probably due to the picrate ion, as solutions of this compound in ethyl- or n-butyl ether, both solvents whose ionizing power has been shown to be very small, are colorless at concentrations up to one-tenth molal. This lends at least qualitative support for the value found for the ionization constant. In the author's opinion, this constant is correct as regards its order of magnitude although the value of the numerical part of the constant may be somewhat greater or less than

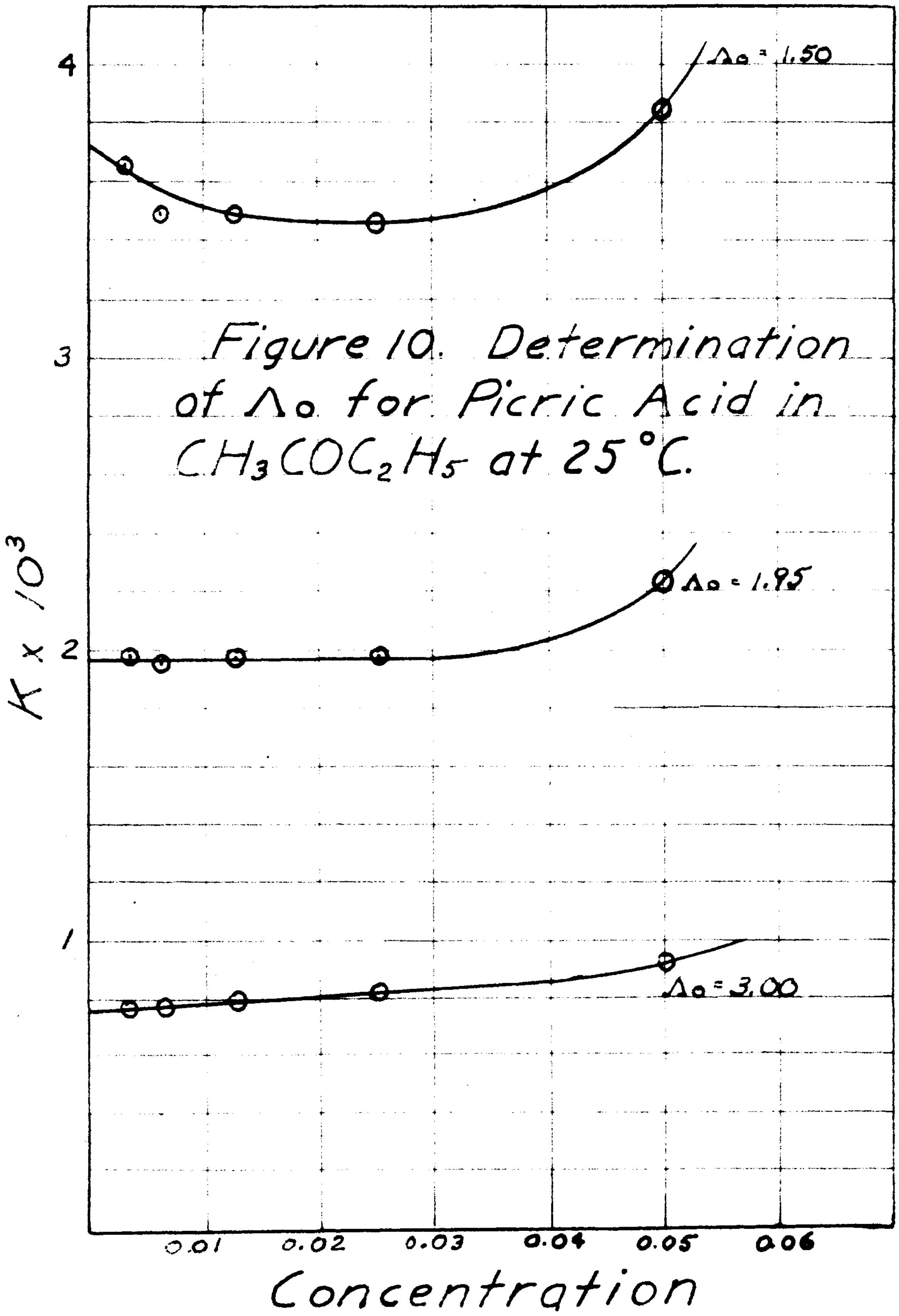


Figure 10. Determination of Λ_0 for Picric Acid in $CH_3COC_2H_5$ at 25 °C.

the value given in Table 11.

The relationship between the ionization constants of picric acid in each of the solvents and the electron-sharing abilities of the R groups is illustrated in Figure 11. On the same coordinates are plotted (dotted line) the ionizations of the acids RCOOH in aqueous solution. This shows clearly that those radicals which, when attached to the carboxyl group, give it a relatively high ionization also decrease the ionizing power of a solvent when they are attached to the solvating group of the solvent molecule.

To facilitate comparison of these results with those obtained cryoscopically there are plotted in Figure 12 the percentage ionizations of picric acid in each of these solvents as a function of the electron-sharing abilities of the R groups. Curves are drawn for the concentrations one- and two-thousandths mole fraction of picric acid. Also plotted on this graph are the values for the dielectric constants of these solvents (dotted line).

Conductance Data and Ionization Constants of Picric Acid in Nitriles

The data obtained for these solutions are tabulated in Tables 12, 13, and 14. The conductances of benzonitrile and propionitrile solutions are represented graphically

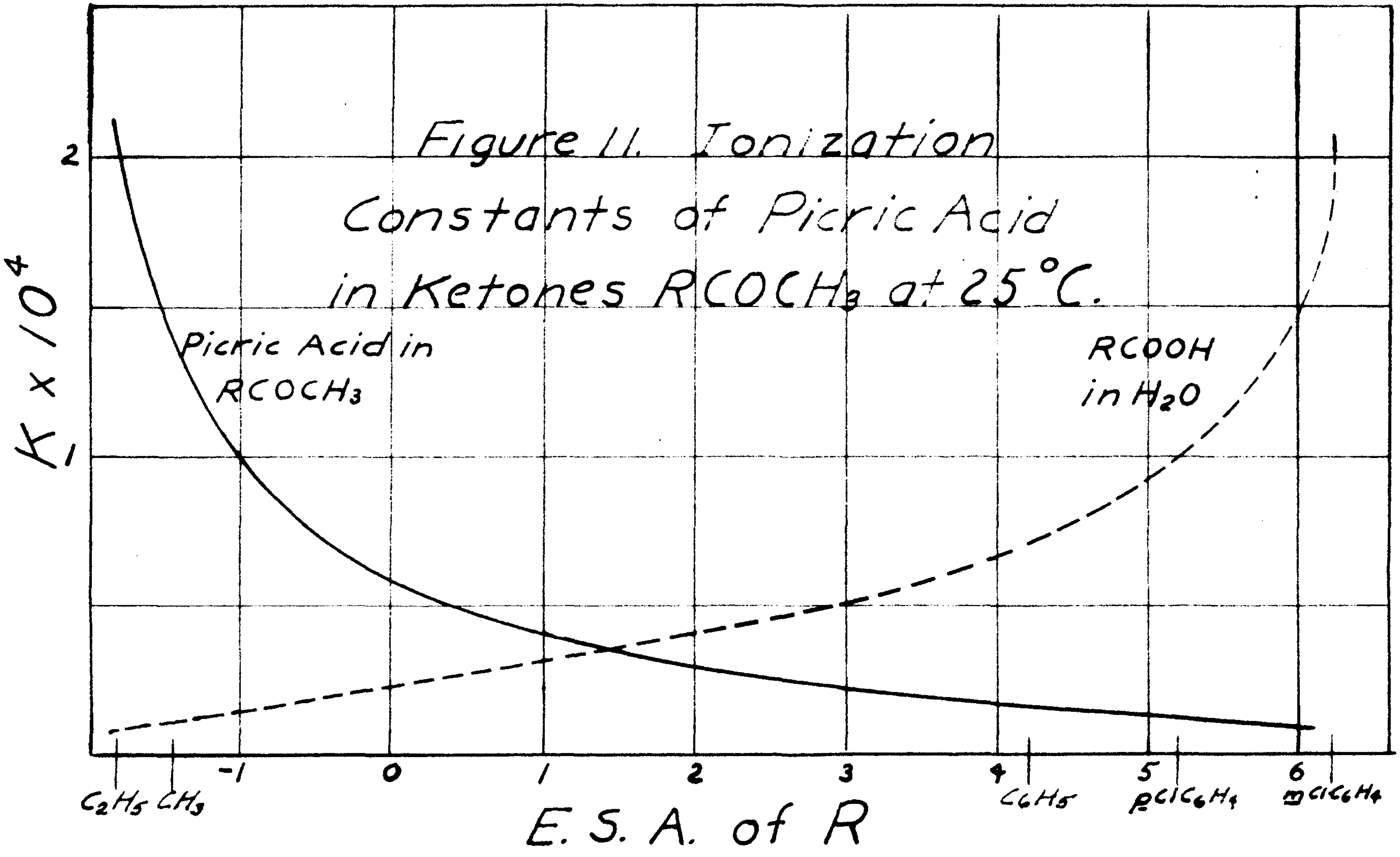


Figure 11. Ionization Constants of Picric Acid in Ketones $RCOCH_3$ at 25°C.

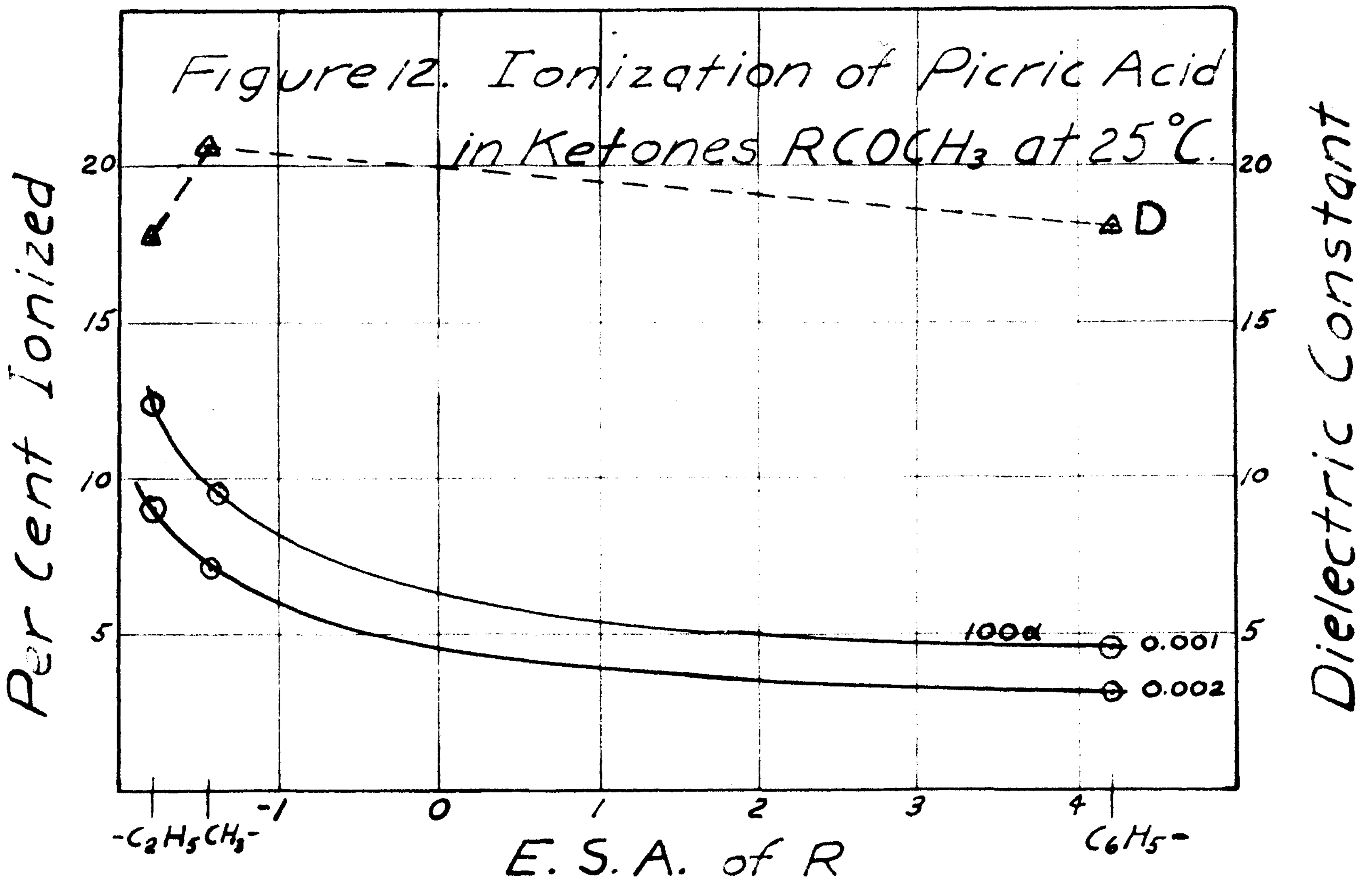


Figure 12. Ionization of Picric Acid in Ketones $RCOCH_3$ at 25°C.

in Figure 13. Since some unusual difficulties were encountered in the course of these measurements, a further discussion is indicated.

Effect of Solvent Association on Rate of Ionization

It will be remembered that in the course of the work on ketones it was discovered that in those solvents where association (via hydrogen bridge formation) was possible, equilibrium was attained much more slowly than in those solvents where such association was impossible. The same phenomenon was observed in the studies on the nitrile solutions. In benzonitrile, where the molecule contains no labile hydrogen, equilibrium was established in three hours. In the case of the propionitrile solutions, almost four days were required for the establishment of equilibrium.

Acetonitrile has the highest dielectric constant of all of the solvents employed, and it should have a comparatively high basicity. In spite of these facts, the ionization in this solvent took place so slowly that no results were obtained. In the opinion of the writer, this is due to the effect of solvent association on the rate of ionization. If the substance is highly associated (as it should be, according to the findings of Landee) and the dissociation into single (solvating) molecules is slow, it is easily seen that the establishment of equilibrium would be slow.

TABLE 12

Conductance of Picric Acid in Benzonitrile at 25°C.

Concentration	Specific conductance	Dilution (cc.)	Equivalent conductance
0.010	359×10^{-7}	0.1×10^{6}	3.59
0.005	261×10^{-7}	0.2×10^{6}	5.22
0.0025	183×10^{-7}	0.4×10^{6}	7.32
0.00125	123×10^{-7}	0.8×10^{6}	9.85
0.000625	82×10^{-7}	1.6×10^{6}	13.11
0.000312	52.8×10^{-7}	3.2×10^{6}	16.90
0.000156	33.8×10^{-7}	6.4×10^{6}	21.60
0.000078	20.5×10^{-7}	12.8×10^{6}	26.25
0.000039	12.3×10^{-7}	25.6×10^{6}	31.50

$\Lambda_0 = 39.6$
$K = 1.02 \times 10^{-4}$

TABLE 13

Conductance of Picric Acid in Phenylacetonitrile at 25°C.

Concentration	Specific conductance	Dilution (cc.)	Equivalent conductance
0.0025	90.3×10^{-7}	0.4×10^{6}	3.61
0.00125	78.8×10^{-7}	0.8×10^{6}	6.30
0.000625	53.9×10^{-7}	1.6×10^{6}	8.62
0.000312	32.4×10^{-7}	3.2×10^{6}	10.38
0.000156	17.7×10^{-7}	6.4×10^{6}	11.30
0.000078	10.2×10^{-7}	12.8×10^{6}	13.17

$\Lambda_0 = 15.05$
$K = 4.8 \times 10^{-4}$

TABLE 14

Conductance of Picric Acid in Propionitrile at 25°C.

Concentration	Specific conductance	Dilution (cc.)	Equivalent conductance
0.005	1360×10^{-7}	0.2×10^{6}	27.2
0.0025	978×10^{-7}	0.4×10^{6}	39.1
0.00125	657×10^{-7}	0.8×10^{6}	52.5
0.000625	412×10^{-7}	1.6×10^{6}	65.9
0.000312	251×10^{-7}	3.2×10^{6}	80.4
0.000156	147×10^{-7}	6.4×10^{6}	94.0
0.000078	84×10^{-7}	12.8×10^{6}	107.5
0.000039	45.1×10^{-7}	25.6×10^{6}	115.5
0.000020	23.3×10^{-7}	51.2×10^{6}	119.2

$\Lambda_0 = 120$
$K = 4.25\times10^{-4}$

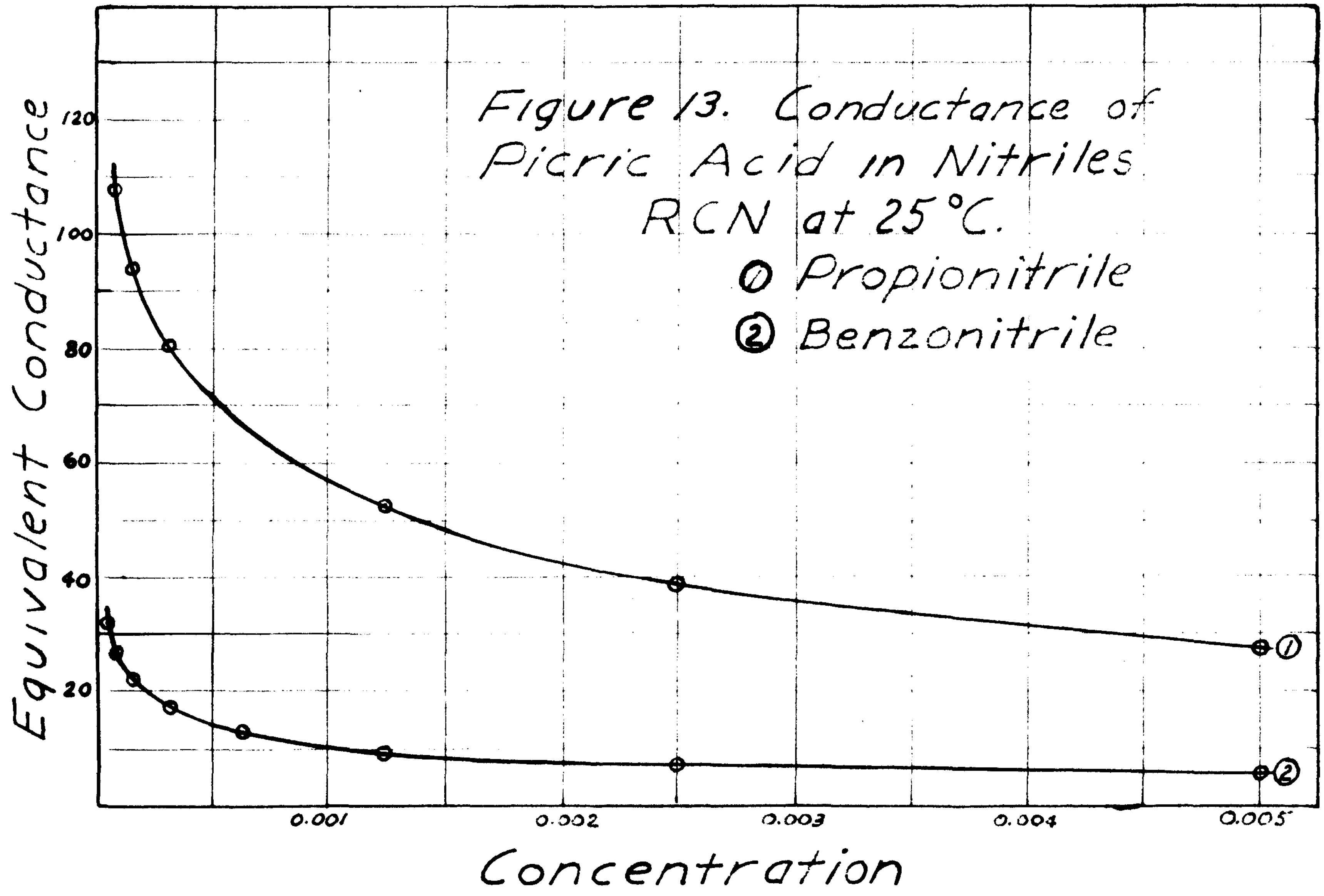


Figure 13. Conductance of Picric Acid in Nitriles RCN at 25°C.

Something of the sort seems to be the case. The solutions were almost colorless when made up, indicating that little ionization had taken place. The color of these solutions deepened very slowly and the conductances increased very slowly also. At the end of a month the conductance was still increasing at about the initial rate. Since there was no indication that equilibrium was near to being attained, determinations in this solvent were abandoned.

Effect of Solvent Association on Conductance

Difficulties of a different nature were encountered in working with phenylacetonitrile. The material first obtained (Eastman) was distilled twice in an atmosphere of purified nitrogen. Its conductance after the second distillation was 1.1×10^{-7} and as this compared favorably with the values in the literature, the solutions were made up, allowed to stand for three days, and their conductances determined. The data obtained on this run are presented in Table 13.

It will be remembered that one of the methods used to determine the conductance at infinite dilution of these solutions consisted of plotting $C\Lambda$ against $1/\Lambda$. In the concentration range where the mass law was obeyed, a straight line was obtained. If anything was wrong with a series of solutions, if the solute or solvent contained any significant impurities, deviations from the straight line were obtained. By the extent of these deviations, if any, was judged the accuracy of the run.

Excellent data (by this criterion) were obtained for the runs in benzonitrile and propionitrile. In the case of the phenylacetonitrile, the deviations were fairly large. Therefore, a second run was attempted. The solvent was recovered by steam distillation, followed by two distillations under reduced pressure in an atmosphere of purified nitrogen exactly as before. The conductance at this point was 2.5×10^{-7}, indicating that the solvent was not quite as pure as before, but still good enough for making a run.

The solutions were made up in the usual manner and were yellow in color, indicating that considerable ionization had taken place. However, the conductance had dropped off tremendously. For example, at a concentration of twenty-five ten-thousandths molar, where the cell resistance had been about twenty thousand ohms, it was now about one hundred seventy thousand ohms at that concentration. Since the apparatus would not measure resistances above about two hundred thousand ohms with any degree of precision, no runs could be made on these solutions.

The only explanation the author can offer concerning this is that there must have been some change in the molecular state of the solution. The fact that ionization had taken place was indicated by the yellow color of the solutions. The color was of about the same intensity as that of the benzonitrile solutions. If the ionization was considerable in both cases, then any such vast change in the conductance must have been due to a change in the ionic velocities. This would indicate that the proton was being solvated by a much larger molecule, probably an association complex of some sort.

It must be admitted that all this is largely conjecture on the author's part. In his studies on association, Turner (65) came to the conclusion that the tendency toward association of organic compounds depended on the presence, in the associating molecule, of certain electronegative groups. These groups are presented below, arranged in the order of their decreasing effectiveness in promoting association.

$$-OH > -CONH_2 > -COOH > -NOH > -CN > -SH > -CSNH_2 > -CSOH > -NH_2 > -CHO$$

It may be seen from the position in this series of the cyanide radical that these nitriles contain groups capable of causing considerable association.

However, no methods above reproach are available for studying the molecular status of pure liquids. All methods for such studies are based on the determination of some physical constant, or constants, of liquids assumed to be normal (as regards their molecular status), such as benzene, carbon tetrachloride, etc. These constants are then compared (by means of empirical equations) with those for other liquids whose molecular status is the subject of study. Deviations are attributed to association or dissociation.

One such equation is the Ramsay-Shields equation, which may be written in the following form:

$$\frac{\gamma_1 (M v_1)^{2/3} - \gamma_2 (M v_2)^{2/3}}{t_1 - t_2} = k$$

where:

γ = surface tension.

M = molecular weight.

v = specific volume.

t = temperature at which a measurement is made.

k = a constant, equal to 2.12 for a large number of "normal" liquids.

Since the value of k is known, it can be used to calculate the molecular weight of an associated liquid if the surface tensions and densities are known for the liquid at two temperatures. Calculations using this equation give the following association indices (association index equals apparent molecular weight/theoretical molecular weight) for a series of nitriles (65).

Acetonitrile............	1.73
Propionitrile...........	1.48
Benzonitrile............	1.02

This is in accordance with the results obtained in this study. Phenylacetonitrile, however, is apparently unassociated according to calculations using this equation.

Another such method for determining molecular weights of liquids is based on Longinescu's relation,

$$\frac{T}{d\sqrt{n}} = K ,$$

where:

T = boiling point in degrees Absolute.

d = density at zero degrees Centigrade.

n = the number of atoms in the molecule or association complex.

K = a constant, equal to 100 for a large number of "normal" liquids.

Calculations using this equation give the following association indices:

Acetonitrile.............	3.3
Propionitrile............	2.3
Phenylacetonitrile.......	1.6
Benzonitrile.............	1.6

Again, these results agree only partially with the explanations advanced above.

Other methods, similar in principle to those discussed above, are reviewed in Turner's monograph. In general, these methods give results agreeing with those presented above. In all cases the order of decreasing association is acetonitrile $>$ propionitrile $>$ benzonitrile. No further data concerning phenylacetonitrile are given, nor are any such data presented in the more recent literature.

However, such methods as those discussed above are not to be taken too seriously. While they may be taken to indicate that association does occur in certain liquids, it is very doubtful if either of these methods or any similar methods give a true measure of the molecular complexity. Agreement among the values obtained by different methods for a given liquid is almost non-existent, and the values given above must be regarded as qualitative evidence at best.

However, all of these methods indicate that acetonitrile is the most highly associated member of this solvent series. Thus, it seems quite probable that the abnormally slow rate of ionization in this solvent can be ascribed to association. As mentioned above, this interpretation is fully supported by the relationships between rate of ionization and possibility for association observed for the other solutions studied.

In view of the scarcity of data concerning the molecular status of phenylacetonitrile, it cannot be said that the explanation advanced concerning the variation in conductance of the solutions in this solvent is either proved or disproved. The rate of ionization in this solvent (for the first run the ionization rate was about the same as that for propionitrile solutions) indicates that there is a considerable amount of association in this solvent. In view of this, the explanation advanced above is at least a reasonable one.

It also seems likely that solvent association affects the extent of ionization as well as the rate at which it takes place and the conductance of the solutions. The nature of this effect will be discussed more fully in a later section of this paper.

DISCUSSION OF RESULTS

Relationship between Ionizing Power of Solvents and Electron-sharing Abilities of Substituent Groups

The results bear out the predictions made in the theoretical portion of this thesis, namely, that those radicals which cause a relatively high degree of ionization when attached to the carboxyl group in acids tend to decrease the ionizing power of a solvent when attached to the functional (solvating) group in the solvent molecule. This relationship is clearly shown in Figure 11. The solid line represents the ionization of picric acid in ketones of the type $RCOCH_3$, and the dotted line shows the ionization in aqueous solution of acids containing these (and other) radicals. It is easily seen that those radicals which have a large electron-sharing ability reduce the ionizing power of the solvent, and vice versa for those radicals which have small electron-sharing abilities.

Effect of Dielectric Constant of Solvent

That the dielectric constant of the solvent cannot be the controlling factor is easily seen from Figure 12. The dielectric constants of these solvents are all about the same, but their ionizing powers are quite different, the ionization constant of picric acid in acetophenone being only about one-tenth of its value in the other two solvents. Further, although acetone has a higher dielectric constant than does methyl ethyl ketone, the latter solvent has the greater ionizing power. Hence, in ionization of this type the dielectric constant of the solvent must be regarded as being of secondary importance.

No curves can be drawn for the values of the ionization constants in the nitriles due to the dubious value of the results in phenylacetonitrile. The results whose accuracy appears adequate, however, support the results obtained using ketones as solvents. In propionitrile (electron-sharing ability of R equals -1.8) the ionization constant is 4.25×10^{-4}, while in benzonitrile (electron-sharing ability of R equals 4.2) the ionization constant is somewhat smaller, 1.0×10^{-4}. The dielectric constants of these solvents are almost exactly the same (benzonitrile 26.5; propionitrile 27.0, both measured at twenty degrees). Hence, the relationships between their ionization constants can be accounted for in terms of the postulates of this thesis, but not in terms of the Nernst-Thomson rule.

Comparison of Inherent Basicities of Functional Groups

A further relationship can be pointed out, which shows the carbonyl group to have a higher inherent basicity than does the cyanide radical. Consider the cases of the solutions of picric acid in methyl ethyl ketone and in propionitrile. While the dielectric constant of the nitrile is considerably greater than that of the ketone, the magnitude of the ionization constants of picric acid in these solvents is about the same. This suggests that the carbonyl group possesses more inherent solvating power than does the cyanide radical. In his studies on association, Landee (40) confirmed a series of functional groups (originally deduced by Auwers) which, when substituted into a solvent molecule, exerted a normalizing influence on the molecular weights of substances dissolved in these solvents; i.e., these groups prevented association of the solute molecules. This series of radicals was as follows:

$$-OH > -COOH > -NH_2 > -CHO > -CN > -COOR > -NO_2 > -X$$

Landee interpreted this normalizing effect as being due to the ability of the solvent to solvate, or associate with, the solute, thus preventing it from associating with itself. This series, as given above, is arranged in decreasing order of normalizing effect, and it shows the carbonyl group (at least in aldehydes) to possess this power to a greater degree than does the cyanide radical. Since ionization, of the type studied in the work described, depends on the ability of the solvent to solvate the acid and then remove the solvated proton, we might well expect that the carbonyl group would have a higher inherent basicity than does the cyanide radical and therefore to be a better ionizing group in a solvent molecule. This appears, indeed, to be the case.

Relationship between Solvent Association and Ionizing Power

The statement was made in connection with the theoretical discussion that the basicity of solvents might be expected to depend, to a certain extent, on the molecular status of the liquid solvent, particularly in regard to the amount of association (via hydrogen bridge formation) of the solvent molecules. A more complete discussion of this effect may be in order here. There cannot be a great deal of doubt that association must play an important part in determining the solvating power of molecules. The results, or rather lack of results, on solutions in acetonitrile, are witness to this fact. Consider the case of a ketone as solvent. It is more or less commonly believed that the maximum covalence of oxygen is three, which means that it can donate one pair of electrons to form one coordinate-covalent bond. This means that, if this valence is used up in association with another solvent molecule, it is no longer available to solvate the proton of an acid and cause it to ionize. This is certainly the case with the nitriles since nitrogen, the donor atom, has only one free electron pair. Thus it would appear that association of the solvent would tend to decrease its ionizing power by cutting down the number of solvent molecules available for solvation. This is somewhat at variance with accepted ideas on this subject since it is widely believed that the more highly associated a solvent is, the greater ionizing power it possesses. The author does not dispute this fact; it is merely his contention that the ionizing power is not because of the association, but rather in spite of it. The very fact that the solvent is highly associated shows that there must be present in its molecule atoms of considerable donor power. The greater the donor power of this atom, the greater ionizing power it might be expected to have, and also the greater would be its association.

It was shown by Landee that association was promoted by the same radicals which inhibited dissociation of an acid, i.e., radicals of small electron-sharing ability. It has been shown in the present study that these same radicals, when substituted into a solvent molecule, increase its ionizing power, other things being equal. Then, granting the assumptions above, these two factors must work against each other. Of the two, the increase in ionizing power due to increased donor power must be the greater, or the relationships shown above would not have been obtained. However, it is obvious that there can be no simple relationship between electronic properties of radicals in the solvent molecule and ionizing power unless the relative contributions of these two factors can be evaluated in some way. Since there is no very good method available for studying the molecular status of liquids, the possibility of such an evaluation is remote.

Although the confirmation of these ideas has not been completely realized, we may cite one piece of evidence in support of them. This concerns the relationship between the ionization constants obtained for the picric acid in the ethyl- and phenyl-substituted ketones and nitriles. In the case of the ketones, where each solvent is capable of association, the ionization constant in the ethyl-substituted compound (methyl ethyl ketone) is about thirteen times as great as it is in the phenyl-substituted compound (acetophenone). In the case of the nitriles, where the ethyl-substituted compound (propionitrile) can associate, while the phenyl-substituted compound (benzonitrile) cannot, the ratio of the ionization constants is only about four to one. The fact that the ionization of the acid in benzonitrile was relatively higher can be explained satisfactorily by the theory discussed above. The donor power of none of its functional groups was wasted in associating with other solvent molecules; all of them were available for solvating the protons.

Comparison of Results with Those Obtained Cryoscopically

Before terminating this discussion, it might be well to consider the relationship between the two sets of results obtained by different methods. The values obtained by the cryoscopic method are much higher than those obtained conductimetrically. There are several reasons why this might be so. First, the solvents used in the cryoscopic determinations were likely not as pure as those used in the conductimetric measurements since the conductance of a substance is a better measure of its purity than is its melting point. Second, in the technique employed in making cryoscopic measurements the solutions were almost continuously exposed to the air. This could not help but result in the absorption of considerable amounts of moisture, and as was shown in the conductimetric work, small amounts of moisture increase the ionization a good deal, at least at lower concentrations. Finally, it is almost certain that in the concentration range which is effective for making cryoscopic measurements (five- to ten-hundredths molal) the solutions are no longer truly "dilute". This may be seen from Figure 10. Here the mass law constant is followed only in the region from zero to twenty-five thousandths molal, and at concentrations above these the constant rises quite rapidly. This would mean that the equations applied to determine the apparent molecular weight would not be strictly applicable in the range in which they were employed.

SUMMARY

1. Theoretical considerations have been presented to show that the ionizing power of a solvent should be an inverse function of the electron-sharing abilities of the radicals attached to the functional (solvating) group, other things being equal.

2. Cryoscopic measurements of the ionizations of picric acid have been made on solutions of the acid in acetophenone, benzophenone, phenyl p-tolyl ketone and propiophenone.

3. Conductimetric measurements have been made on the ionizations of picric acid when dissolved in acetone, acetophenone, methyl ethyl ketone, benzonitrile and propionitrile.

4. It has been pointed out that the rate of ionization of the acid is greatly affected by association of the solvent molecules.

5. The data obtained by the above measurements have been shown to substantiate the postulates put forth in the theoretical part of this thesis.

6. A theoretical discussion has been presented in an attempt to clarify the relationship between the association of a solvent and its ionizing power.

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