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The effect of the solvent upon the polar properties of organic compounds

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THE EFFECT OF THE SOLVENT UPON THE POLAR PROPERTIES

OF ORGANIC COMPOUNDS

BY

Lyle David Goodhue

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In charge of Major work

Head of Major Department

Dean of Graduate College

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INTRODUCTION

In previous studies from the Plant Chemistry Laboratories, a mathematical relationship has been demonstrated between the relative affinities of different organic radicals attached to the same polar grouping. In order to arrive at this generalization, a considerable number of equilibria have been measured for reactions involving organic compounds. The measurements were made in the solvent most suitable for the particular reaction. The constants for the primary amines and for the acids (20), for the α-substituted pyrrolines and pyrrolidines (7)(27), for the arsonic acids (28), and for a number of other compounds were measured in water solutions. The equilibrium constant for the reaction

$$2RHgI \rightleftharpoons R_2Hg + HgI_2$$
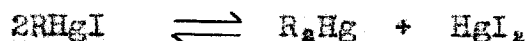
and the ionization constants for the organo-mercury nitrates (21)(22) were determined in absolute ethyl alcohol. The equilibrium constants for the reaction between chloral and a series of mercaptans to form the hemimercaptal were determined in benzene (23). Although this work would appear to be quite extensive, complete data for any one series have not been available in more than one solvent. The following investigation has been undertaken to determine the effect of the solvent upon the polar properties of organic compounds.

A recent discussion of the role of the solvent in acid-base equilibria was given by Hall (17) at the Cincinnati symposium on non-aqueous solutions. Opinion regarding the solvent

influence on the physical properties of the solute may be
divided into two divergent schools. The summary of Brønsted
(3) would indicate that the solvent influence is a constant and
additive factor at least for acids and bases in alcoholic
solution. Conant (6), however, considers that the simplest
relationships between the structures of compounds and the free
energy changes of their reactions will be found in the gaseous
state. The data which Conant considers would indicate that the
disturbing influence of the solvent might introduce irregular-
ities as large as 1000 calories in the measurements of the free
energies of a reaction.

It is apparent that an attempt to compare the relative
affinities of organic radicals by measuring the electrical
properties of polar groupings attached to these radicals can
not be successful if the solvent influence on the free energies
of the polar groupings is erratic. As previously stated (20),
if the electronic concepts of valence are at all correct it
would be expected that the variations in the electrical
properties of any polar grouping could be expressed as a
function of the electron sharing ability of the organic radical
attached to it. If the polar grouping formed a complex with
the solvent, this complex likewise would be expected to be of
a characteristic structural type for that particular polar
grouping and solvent. The free energy of the polar grouping
with its solvent complex would still be expected to be a
function of the electron sharing ability of the organic radical

since this is the only variable factor affecting the polar
grouping. The energy level of the complex would be expected to
be different from that of the free polar grouping and from that
in different solvents. Erratic or irregular influences due to
the solvent would be expected only if the radical contained
groupings other than the polar grouping which united with the
solvent. If these latter complexes did not themselves
dissociate to form electrically charged bodies which would
interfere with the measurements for the polar grouping,
disturbing influences would be expected only if the second
union were located with but four[1] or less atoms between it and
the polar grouping.

As pointed out by Brønsted (3), the data of Goldschmidt
indicate that the solvent influence is constant and additive
for the acids and primary amines in water, methanol and ethanol
solutions. Accordingly, it would be expected that the
dissociation constants for these two series of compounds in
methanol and ethanol solutions would give curves parallel to
the water curves when treated by the graphical method previously
used (20) for demonstrating that the aqueous values could be
expressed as a mathematical function of the electron sharing
ability of the organic radicals.

Goldschmidt's (13)(14)(15) data for the comparative basic

[1]This statement is based on the fact that the influence of the
most negative radicals seem to be completely absorbed before
transmition through four carbon atoms.

strengths of the acids and amines were obtained by the measurement of the degree of alcoholysis of the salts using conductimetric methods. Although great care was used to justify this method by the measurement of different combinations of acids and amines and by application of the method to previously measured salts in water solutions, the data are subject to the general disfavor which is accorded all conductimetric data at the present time. For this reason and also for comparative purposes in extending the measurements to other compounds, it seemed advisable to compare some of Goldschmidt's values with values obtained by the potentiometric method using a hydrogen electrode in methanol and ethanol solutions. A series of four α-substituted pyrrolidines was also measured in methanol to demonstrate that the constant influence of the solvent was not limited to the structures characterized by the primary amines and acids.

DISCUSSION OF METHOD

The measurement of cells in non-aqueous solvents has been quite limited due probably to the difficulties associated with measurements of cells of extremely high resistance. Also the effect of water on the measurements, the insolubility of the salts and the evaporation of the solvent have done much to turn workers away from this problem.

Although electrometric methods have been used in mixed solvents to determine dissociation constants almost no definite values have been reported in pure solvents. Only recently Hartley (5)(24) has reported the value of an easily reproduceable reference electrode and has shown that the hydrogen electrode can be used successfully in both methyl and ethyl alcohol.

Preliminary studies were made to eliminate using the apparently troublesome hydrogen electrode. The glass electrode was tried and found to be very unsatisfactory. Later Dole (9) pointed out that this electrode is not dependable in solutions where the water activity is extremely low. The quinhydrone electrode in alcohol could not be made to yield a steady potential in confirmation of the attempts of Buckley and Hartley (5).

The hydrogen electrode was finally adopted and in connection with a vacuum tube potentiometer has proved to be a very valuable tool in the determination of dissociation constants in alcoholic solutions. The values reported here are obtained by measuring the hydrogen ion activity of the half-neutralized alcoholic

solutions directly analogous to the method used in water. The
results are subject to some correction as soon as sufficient
data are made available to calculate ion activities.

While this investigation was in progress, Harned and
Ehlers (18) published a very accurate method for determining
the dissociation constant of acetic acid in water solutions.
By measuring the cell

$$Pt/H_2(1 \text{ atm}) \text{ HAc}(m_1) \text{ NaAc}(m_2) \text{ NaCl }(m_3) \text{ AgCl/Ag}$$

at a number of different concentrations and extrapolating
certain functions to zero ionic concentration, he obtained the
corrected dissociation constant. It is necessary to know only
the standard electrode potential of the silver-silver chloride
electrode at the desired temperature and an approximate value
of the dissociation constant of the acid. Since these values
are now known in both methanol and ethanol, it is quite
probable that accurate values for the dissociation constants
could be obtained in these solvents. In using this method it
is not necessary to know the ion activities since they appear
as a ratio which is very close to unity and becomes unity upon
extrapolating to zero concentration.

EXPERIMENTAL PART

The Measurement of a Series of Acids and Amines in Methanol

Construction of Apparatus

The high resistance of alcoholic solutions causes considerable difficulty in the measurement of the E.M.F. of cells by the ordinary methods. A vacuum tube potentiometer arrangement designed for elimination of this difficulty with the glass electrode in water solutions was found equally satisfactory for cells in methanol solutions. The instrument employed was developed by Goodhue, Schwarte and Fulmer (16) and constructed according to the diagram in Figure 1.

All measurements were made in an air bath controlled by a sensitive DeKhotinsky regulator to $25°C \pm 0.1$. The cabinet was lined with copper gauze which was grounded to prevent interference by the alternating current used in the heating units. This shielding is not necessary when the E.M.F. of low resistance cells is measured. The Weston cell used was checked against two cells certified by the Bureau of Standards.

Preparation of Materials

The absolute methyl alcohol was prepared similar to the method of Hartley and Raikes (19). This method consists of a careful fractionation of 99 per cent synthetic methanol through a three foot Hempel column, drying with aluminum amalgam and finally distilling from freshly prepared anhydrous copper sulfate. Alcohol prepared in this way had a density of 0.7866 ± 0.0001 as compared to pure methyl alcohol with a density of

TO GLASS ELECTRODE

TO CALOMEL CELL
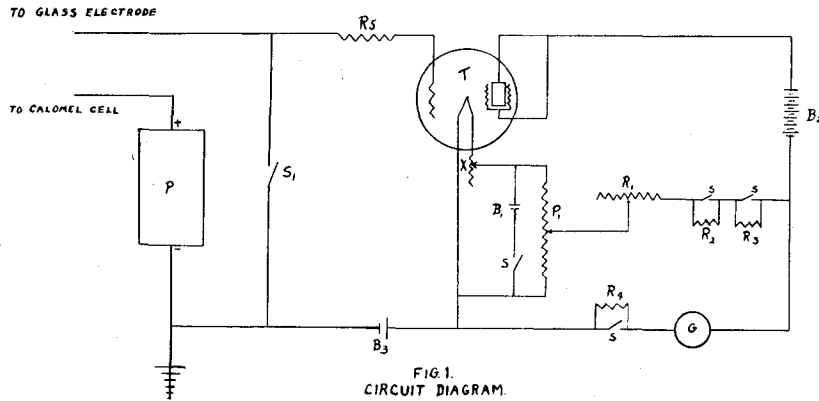
FIG.1.
CIRCUIT DIAGRAM.

B_1	——	2 VOLT STORAGE CELL
B_2	——	22½ VOLT "B" BATTERY
B_3	——	1½ VOLT DRY CELL
G	——	GALVANOMETER
P	——	POTENTIOMETER
P_1	——	400Ω POTENTIOMETER
R_1	——	10,000Ω VARIABLE RESISTANCE
R_2+R_3	—	20,000Ω FIXED RESISTANCE
R_4	——	¼ MEGOHM FIXED RESISTANCE
R_5	——	10 MEGOHM " "
S	——	SWITCHES
S_1	——	GRID SWITCH
T	——	UX232 ELECTRON TUBE
X	——	30Ω FILAMENT CONTROL
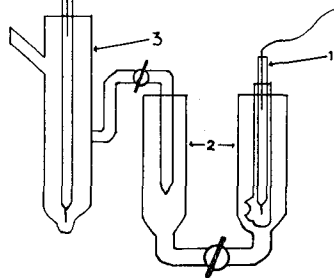
FIG. 2

1	——	Ag-AgCl ELECTRODE
2	——	KCl BRIDGE
3	——	CALOMEL HALF CELL.

Figure 1.

The above diagrams are from the publication by Goodhue, Schwarte and Fulmer (16). The lower figure shows the construction of a glass electrode.

0.7864 at 25°C. The water content was also checked roughly by adding calcium carbide, filtering and treating with ammonical cuprous chloride. The amount of red color developed was a measure of the water content. Hartley and Raikes recommend this test for methyl alcohol but state that it is not satisfactory for ethyl alcohol. The alcohol was stored in stoppered Erlenmeyer flasks. After the first few runs, synthetic methanol was used since no difference could be detected in the results with alcohol from the two different sources.

In the primary amine series, the o-chlorobenzylamine was prepared by the method of Franzen (12). The oxime of o-chlorobenzaldehyde was prepared and reduced with zinc dust and acetic acid. The hydrochloride of the amine was prepared by passing hydrogen chloride gas into an alcholic solution of the free amine from which the salt crystallized very easily upon cooling. After several crystallizations potassium hydroxide was added to a portion of the hydrochloride and the free amine was dried, distilled, and sealed in small tared ampules. The amine readily forms the carbonate from the carbon dioxide in the air.

The other amines and acids were purified either by crystallization or fractional distillation from purchased stocks. The substituted pyrrolidines were furnished by Starr and Bulbrook (27) of this laboratory. In the amine series the half-neutralized solutions of the more basic members were prepared by weighing equivalent molal quantities of the free base in ampules and the hydrochloride salt. The half neutralized solutions of

the amines less basic than p-toluidine had to be prepared by adding half the equivalent amount of an alcoholic hydrogen chloride solution that had been previously standardized against a known base in water solution. Solutions of p-toluidine were prepared by both methods and the results were found to agree very closely. The alcoholic hydrogen chloride is not stable due to esterification and must be used within a few hours after preparation. Hartley has found that the rate of esterification is 0.25 per cent per day at 25° C.

In the acid series, benzoic, p-toluic and p-bromobenzoic acids form stable half-neutralized salts which can be purified by recrystallization from alcohol. They are described by Farmer (11) who prepared them by completely neutralizing a quantity of the free acid dissolved in alcohol with potassium hydroxide, and then adding another equal quantity of acid. Upon cooling, the acid salts were easily crystallized. They were dried over phosphorus pentoxide and checked for purity by titration. In the other cases, the half-neutralized solutions were prepared by weighting equal molal quantities of the free acid and the sodium or potassium salt.

All solutions were made up by weight, and the concentrations were expressed in terms of molalities. The hydrogen-ion activity of the solutions was measured within three hours after preparation. Repeated tests showed no detectable difference in the hydrogen ion activity of these solutions after five hours indicating that esterification is not appreciable under these

conditions. Measurements on solutions one day old usually showed a change of about 0.05 pK units.

Reference Electrodes.

The calomel half cells in methanol were not constant and although convenient to use as reference electrodes they must be standardized. The silver-silver chloride electrode was used for the purpose as recommended by Buckley and Hartley (5). The silver electrodes were prepared by the electrolytic method of MacInnes and Beattie and were chloridized in a 0.1 m solution of sodium chloride in methanol using a current density of five milliamperes per electrode for twenty minutes. The electrodes were always prepared in duplicate and were reproduceable to ± 0.2 millivolt.

Recently Brown (4) has shown that silver deposited from a solution of pure potassium silver cyanide produces a superior electrode. While this method does not change the initial E.M.F., the life of the electrode in alcoholic solutions was found to be greatly increased.

The calomel half cells with 0.1 m sodium chloride in methyl alcohol used as reference electrodes were always maintained at least in duplicate. The E.M.F. of the salts measured against the silver-silver chloride electrode dropped during the first month from 0.0475 to 0.0457 volts. Two of these cells after being used by a number of individuals without special precautions over a twelve month period had an E.M.F. of 0.0458 and 0.0465 volts. Buckley and Hartley report the value of the silver-silver

chloride electrode as +0.0711 volts when referred to the normal hydrogen electrode in methanol as zero. This value should be added to the above values of the calomel half cells to give their voltages in reference to the normal hydrogen electrode in methanol. The calomel half cell has been used for all measurements in methanol.

After working in ethyl alcohol it was found that a half cell of the type

$$Hg \ / \ HgI_2(c_1) \ KI(c_2) \ //$$

is very easily prepared and can be readily duplicated to ± 0.2 millivolts. Concentration cells of this type (22) in ethanol solutions remain constant for several months.

To test the precision to which these cells could be duplicated in methyl alcohol, two half cells containing different molalities of mercuric iodide were prepared and measured against each other. The cell

$$Hg \ / \ HgI_2(0.01 \ m) \ KI(0.05 \ m) \ // \ KI(0.05 \ m) \ HgI_2(0.005 \ m) \ / \ Hg$$

was measured at intervals over a period of one month and the voltage, 0.0137, was found to be constant to 0.2 millivolts. New cells prepared at the end of a month and checked against the old ones of the same concentration showed no more change than 0.2 millivolts.

The value of these cells referred to the normal hydrogen electrode in methanol was determined by measuring the voltage against the silver-silver chloride electrode similar to the

procedure for the calomel half cell. Electrodes prepared by the method of Brown (4) gave the value 0.2737 volts. Since the mercuric iodide half cell is negative to the hydrogen electrode, 0.0711 volts must be subtracted from the above value to obtain the value for the mercuric iodide half cell. If the liquid junction potential is calculated according to Hartley (1) (5), by substituting the mobilities of the ions in methanol, in the ordinary equations for water solutions, a value -0.0026 volts is obtained. Therefore the true voltage of the 0.005 m mercuric iodide half cell in 0.05 m potassium iodide is -0.2052. In calculating the liquid junction potentials, the small concentration of mercuric iodide was neglected since there were no formulas for complex salts such as were formed in this case. All junctions were made through ground glass stoppers or stopcocks and were renewed by flushing after each measurement.

Preparation of Hydrogen Electrode.

Both palladium and platinum black were used as catalysts for the hydrogen electrode. Identical potentials were obtained with both catalysts with compounds not capable of being reduced. It was found impossible to measure the pyrrolines which contain one double bond when platinum black was used as the catalyst. It was found later that palladium black reduces this double bond very slowly and a fair value of the dissociation constants of the pyrrolidines may be obtained. Also, palladium black gave excellent results with compounds such as aniline or p-toluidine containing the benzene ring while the results with platinum

black were irregular. Some compounds such as m-chloroaniline were attacked more rapidly by palladium. Both catalysts were too active to give satisfactory results with nitro compounds or the chloroacetic acids, reduction being extremely rapid.

Small platinum flags about five millimeters square were used for both catalysts. The platinum black was deposited from a three per cent platinic chloride solution containing a trace of lead acetate, using a current density of 0.2 amperes per electrode for three or four minutes. The palladium black was deposited in the same way from a one per cent palladium chloride solution in strong hydrochloric acid containing a trace of lead acetate. The electrodes were electrolyzed in dilute sulfuric acid for five minutes, washed several times in 99 per cent methanol, then in absolute methanol several times to remove traces of moisture.

The cells containing the hydrogen electrodes were constructed so that the hydrogen bubbled from the bottom over the flags which were kept entirely submerged in the solution being measured. (See Figure 2.) The compartment containing the two hydrogen electrodes was connected by a stopcock, kept closed to prevent any mercury salts reaching the hydrogen electrodes, to another into which the reference electrode dipped. The two electrodes were held in place by a rubber stopper which had been previously freed from uncombined sulfur. The hydrogen gas was saturated with methyl alcohol before entering the cell and was used directly. The purity of the hydrogen from each new cylinder was determined by checking the voltage obtained with

Figure 2

a. Trap containing alcohol
b. Hydrogen inlet
c. Ground glass stopper
d. Calomel or mercury-
   mercuric iodide
   half cell
e. Mercury seal
f. Rubber connections
g. Calcium chloride tube

the hydrogen electrode in a 0.05 molar potassium acid phthalate
solution in water. The voltage obtained with palladium
electrodes against a saturated calomel half cell in water was
0.4805.

Unless complicated by reduction reactions, the cells came
to equilibrium in a few minutes and have often remained
constant to ±0.5 millivolts for five hours. The results were
rejected if the two electrodes did not agree within 0.5 milli-
volt. The electrodes did not poison easily and could be used
repeatedly, but to eliminate any uncertainty, they were freshly
prepared before each measurement.

Elimination of Liquid Junction Potentials.

The junction between the hydrogen half cell and the
calomel half cell was made through a glass stopper kept closed
all of the time. Partington and Simpson (26) have shown that
liquid junction potentials in concentration cells of sodium
iodide in ethyl alcohol can be eliminated by a bridge of
saturated potassium thiocyanate. Buckley and Hartley (5) have
used a saturated solution of sodium iodide in methyl alcohol
but without completely eliminating the liquid junction
potentials. In a number of cases during this investigation, a
saturated potassium thiocyanate or sodium iodide bridge was
introduced after the cell had come to equilibrium. In no case
was the voltage changed by more than one millivolt by these
changes in type of junction.

Tables of Data in Methanol.

The data for the series of organic acids in methanol are
reported in Table I. The E.M.F. recorded for each concentration
is the average of two hydrogen electrodes agreeing to 0.5
millivolts or less. The concentrations recorded also include
the combined acid and are expressed in terms of molalities.
Similar values are reported in Table II for a series of primary
amines and α-substituted pyrrolidines. These tables include
all determinations and not a selected few that agree within this
range. An attempt was made to measure ethyl pyrroline using
platinum black as the catalyst for the hydrogen electrode.
The voltage rose very rapidly until the value for the corres-
ponding pyrrolidine was reached. This rapid reduction by the
hydrogen electrode had been made the subject of another
investigation and it suffices to say that the pyrrolines can be
measured with palladium black as the catalyst and that these
values will be reported later.

Measurement of Acids and Amines in Ethanol.
Construction of Apparatus.

Due to the decreased activity of the ions in ethanol, the
resistance of solutions in this solvent is so great that the one
electron tube potentiometer used for methanol solutions was not
satisfactory. Accordingly, a four tube outfit described by
Ellis and Kiehl (10) was constructed and found to give excellent
satisfaction. This instrument gave a precision of ±0.1
millivolts across an estimated resistance of more than a billion

Table I.

E.M.F. of Cells for a Series of Organic Acids in Methanol

Pt/H$_2$ (1 atm) Acid // NaCl (0.1 m) Hg$_2$Cl$_2$/Hg
salt

Substance	Total Concentration	E.M.F. corr. to 760 mm.	-log a$_H$
Acetic acid	0.0382	0.6688	9.33
	0.0346	0.6702	9.36
p-Toluic acid	0.0411	0.6683	9.33
	0.0428	0.6683	9.33
Benzoic acid	0.0400	0.6554	9.11
	0.0545	0.6558	9.12
p-Bromobenzoic acid	0.0340	0.6630	8.73
	0.0346	0.6635	8.74
m-Chlorobenzoic acid	0.0447	0.6237	8.55
	0.0531	0.6225	8.58

Table II.

E.M.F. of Cells for a Series of Primary Amines and α-Substituted Pyrrolidines in Methanol

Pt/H_2 (1 atm) Amine // NaCl (0.1 m) Hg_2Cl_2/Hg
salt

Substance	Total Concentration	E.M.F.	$-\log a_H$	$-\log K_{MeOH}$
n-Butylamine	0.0972	0.8113	11.78	4.92
	0.0606	0.8120	11.79	4.92
o-Chlorobenzylamine	0.0751	0.7152	10.16	6.61
	0.0524	0.7154	10.16	6.61
p-Toluidine	0.1001	0.5132	6.74	9.97
	0.0600	0.5123	6.73	9.98
	0.0536	0.5100[1]	6.68	10.02
	0.0217	0.5106[1]	6.69	10.00
Aniline	0.0635	0.4792	6.17	10.54
	0.0644	0.4803	6.19	10.52
m-Chloroaniline	0.0361	0.3839	4.55	12.15
	0.0589	0.3854	4.58	12.13
α-Cyclohexylpyrrolidine[2]	0.0359	0.8123	11.81	4.90
	0.0334	0.8140	11.84	4.87
α-Benzylpyrrolidine	0.0413	0.7820	11.29	5.42
	0.0317	0.7823	11.29	5.42
α-(p-Tolyl) pyrrolidine	0.0239	0.7682	11.05	5.66
	0.0310	0.7662	11.02	5.69
α-Phenylpyrrolidine	0.0396	0.7576	10.87	5.83
	0.0381	0.7572	10.87	5.83

[1]These values were determined independently by C. L. Mehltretter. These solutions and the remaining ones below were made by half neutralizing the amine with HCl in methyl alcohol. The solutions above this point were made from equal molal quantities of the amine and its hydrochloride salt.

[2]The α-substituted pyrrolidines were prepared in this laboratory by Helen Bulbrook and D. F. Starr (27).

ohms. They present data showing good precision up to 100,000 megohms.

Preparation of Absolute Methanol.

Absolute alcohol from purchased stocks was fractionated twice using a three foot Hempel column. In each case the first and last third was rejected. The specific gravity of a typical sample was found to be 0.78743 compared with 0.78736 for pure alcohol at 25° C.

Reference Electrodes.

The standard electrode potential of the silver-silver chloride electrode has been reported by MacFarlane and Hartley (24) thus making possible the measurement of hydrogen-ion activities in this solvent. Though reproduceable, these electrodes are not constant for more than a few days at the most and cannot be relied upon for more than one day. The calomel half cell was not constant and was not recommended. In view of these facts, the author decided to use one of the mercury-mercuric iodide half cells reported by Johns and Hixon (22). These cells were shown by them to be constant to ±0.1 millivolts for at least one month. To confirm these data, two half cells forming the cell

Hg/HgI_2 (0.005 m) KI (0.05 m) // KI (0.05 m) HgI_2 (0.01 m)/Hg were prepared and the E.M.F. measured. The value obtained, 0.0146 volts, remained constant to ±0.1 millivolts for six weeks. The value given by Johns and Hixon was 0.01455 volts. At the end of one month a new half cell with a concentration of 0.005 m

HgI_2 was made up and its E.M.F. measured against the old half cell of the same concentration was found to be 0.0000. These data indicate the advantage of these half cells as reference electrodes if the E.M.F. referred to the normal hydrogen electrode in ethanol could be determined. This has been done in two different ways: first, by measuring against the silver-silver chloride electrode in a 0.01 m lithium chloride solution, and second, by using the hydrogen electrode in an alcoholic solution of hydrogen chloride.

The average of ten closely agreeing values for the cell

$$Hg/HgI_2(0.005 \text{ m}) \text{ KI}(0.05 \text{ m}) \text{ // } LiCl(0.01 \text{ m}) \text{ AgCl/Ag}$$

was found to be 0.3098 volts. The mobilities of the ions given by Barak and Hartley (1) were used to calculate the liquid junction potentials; the value obtained was -0.0049 volts, using the formula for water solutions. The 0.01 m silver-silver chloride has been calculated by MacFarlane and Hartley (24) to be 0.0594 volts positive to hydrogen, therefore:

$$-0.3098 -0.0049 +0.0594 = -0.2553 \text{ volts}$$

which is the value of the mercuric iodide half-cell referred to hydrogen as zero in ethanol.

The above figure was checked against a 0.169 m solution of hydrogen chloride in alcohol. The E.M.F. of the cell at a pressure of 760 mm.

$$Pt/H_2(1 \text{ atm}) \text{ HCl}(0.169 \text{ m}) \text{ // } KI(0.05 \text{ m}) \text{ } HgI_2(0.005 \text{ m})/Hg$$

was -0.1431. The voltage for the hydrogen half cell, -0.0853, was calculated from the activity data of Woolcock and Hartley (29) and the value, -0.0262 volts, for the liquid junction

potential was calculated by the method described for the
preceding cell. Therefore:

$$-0.1431 -0.0853 -0.0262 = -0.2546 \text{ volts}$$

which is in good agreement with the value obtained by the first
method. The value -0.2550 has been used to calculate the
hydrogen ion activities in ethanol.

The preparation of the compounds and their solutions, and
the technic of measuring the hydrogen ion activity was
exactly as described for the measurements in methanol.

Tables of Data in Ethanol.

The data for the series of acids are reported in Table III
and for the amines in Table IV. The total concentrations are
expressed in terms of molalities.

The Behavior of the Hydrogen Electrode.
Action of Platinum Black on Potassium Acid Phthalate.

Considerable difficulty is often encountered in the prepar-
ation of a good hydrogen electrode, especially if the voltage
is checked in a potassium acid phthalate buffer solution. In
a number of cases in this laboratory it has been found impossible
to obtain the voltage corresponding to a pH of 3.97 using
potassium acid phthalate when platinum black is used as the
catalyst. Repeated attempts to obtain a more active catalyst
have only ended in an apparently poisoned electrode. In spite
of this fact, these same electrodes gave correct readings in
phosphate and acetate buffers. To account for the poor results

Table III.

E.M.F. of Cells for a Series of Organic Acids in Ethanol

Pt/H_2 (1 atm) Acid // KI (0.05) HgI_2 (0.005 m)/Hg

Substance	Total Acid Concentration	E.M.F. corr. to 760 mm.	-log a_H
Acetic acid	0.0106	0.3589	10.39
	0.0212	0.3563	10.35
p-Toluic acid	0.2000	0.3600	10.41
	0.2000	0.3597	10.40
Benzoic acid	0.2000	0.3460	10.17
	0.2000	0.3478	10.20
p-Bromobenzoic acid	0.2000	0.3149	9.64
	0.2000	0.3154	9.65
m-Chlorobenzoic acid	0.2000	0.3106	9.57
	0.2000	0.3089	9.54

Table IV.

E.M.F. of Cells for a Series of Primary Amines in Ethanol

Pt/H_2 (1 atm) Amine // KI (0.05) HgI_2 (0.005)/Hg
salt

Substance	Total Amine Concentration	E.M.F. corr. to 760 mm.	$-\log a_H$	$-\log K_{EtOH}$
n-Butylamine	0.0322	0.4391	11.74	7.40
	0.0325	0.4409	11.77	7.37
o-Chlorobenzylamine	0.0210	0.3341	9.97	9.17
	0.0206	0.3338	9.96	9.18
p-Toluidine	0.0209	0.1436	6.75	12.39
	0.0163	0.1412	6.70	12.44
Aniline	0.0482	0.1108	6.19	12.95
	0.0323	0.1115	6.20	12.94
	0.0329	0.1104	6.18	12.96
m-Chloroaniline	0.0393	0.002[1]	4.35	14.79
	0.0422	0.001[1]	4.33	14.81

[1]These values are probably somewhat low due to the rapid reduction by the hydrogen electrode.

in potassium acid phthalate the possibility of reduction of the benzene ring has suggested itself, and since palladium does not reduce the benzene ring, an electrode using this catalyst should give the correct voltage. This has been found to be true. Electrodes using palladium black have always given correct readings not only in 0.05 m potassium acid phthalate but in phosphate and acetate buffers as well. The apparently poisoned electrodes, using platinum black were probably too active instead of not being active enough. This conclusion is supported by the fact that an old hydrogen electrode often gives better values in potassium acid phthalate than a fresh one.

The Specific Action of Palladium Black.

Before this specific action of the different catalysts was noted, considerable difficulty was encountered in measuring compounds containing the benzene ring in alcoholic solutions. In fact, the reduction is much more rapid in alcohol than in water. Using palladium black, very good readings could be obtained on aniline, p-toluidine, and n-butylamine in both methyl and ethyl alcohol. Platinum black gave identical readings on n-butylamine but always gave low readings with aniline and p-toluidine. Compounds containing a substituted halogen are always difficult to measure in both methyl and ethyl alcohol and are often reduced so rapidly that no measurement can be made at all. With the more inactive halogens a better reading can usually be obtained with platinum black since palladium is known to be a good catalyst for the reduction of

halogen compounds. Accordingly, platinum black has been used to measure the dissociation constants of o-chlorobenzylamine, and m-chloroaniline in the amine series, and m-chloro- and p-bromobenzoic acids in the acid series.

It has been found more difficult to obtain good results with the acids in ethyl alcohol than it is in methyl alcohol. For example: a half neutralized solution of benzoic acid in methyl alcohol will give a perfectly definite and constant reading, but in ethyl alcohol this is not true. Even acetic acid does not give satisfactory measurements in ethyl alcohol. The only possible explanation is that a small amount of ester is formed and this is reduced by the hydrogen electrode. In the case where methyl alcohol is the solvent, either no ester is formed or the methyl ester is not as easily reduced. Halogen compounds appear to reduce more rapidly in ethyl alcohol, suggesting that reduction of any reduceable compound might take place more rapidly in ethyl alcohol. This point was checked by reducing ethyl pyrroline in both solvents with the hydrogen electrode and following the change in voltage with the potentiometer. During the most rapid part of the reduction the voltage rose 26 millivolts per minute in both cases.

Qualifications of a Good Hydrogen Electrode.

If the hydrogen electrode is functioning properly in alcoholic solutions the duplicate electrodes should agree to 0.5 millivolts or less. Also, after the electrodes have come to equilibrium the voltage should not change more than 0.5

millivolts when the flow of gas is interrupted, and last,
the voltage should not fluctuate or change with the rate at
which the gas is bubbled through the solution. These ideal
conditions are easily realized with compounds not readily reduced
by the hydrogen electrode.

Even though difficulty was experienced in the measurement
of the dissociation constants of some compounds, except for
m-chloroaniline in ethyl alcohol, all the values obtained are
well within 0.1 pK units as far as measurement is concerned.
The value obtained for m-chloroaniline is close to the value
given by Goldschmidt but it is doubtful if the maximum voltage
is ever reached.

DISCUSSION OF RESULTS

Calculation of Results.

The experimental procedure used for the alcoholic solutions is directly analogous to the procedure for determining the ionization constants for weak organic acids and primary amines in water solutions. The calculations of the ionization constants for methanol and ethanol have likewise been made directly parallel to the corresponding calculations for water solutions. The values obtained in this way are subject to further precision as a more refined technic is developed and a more extensive knowledge of ion activities in methyl and ethyl alcohol is made available.

The hydrogen ion activities were calculated by the equation

$$-\log a_H = \frac{E}{0.0591}$$

which is analogous to the equation for water solutions. In the case of methanol solutions where the calomel half cell was used as the reference electrode E is obtained by subtracting the value of this electrode from the recorded voltages in tables I and II. As previously stated, this value is not constant and must be determined at intervals against a fresh silver-silver chloride electrode. The voltage was found to be 0.1148 during the time the amines were measured and 0.1169 volts when the constants for the acids were determined.

In the case of the ethanol solutions the value of the

mercuric iodide half cell is 0.2550 volts negative to hydrogen. Therefore, this ammount must be added to the recorded voltages in Tables III and IV to obtain E in the above equation.

The ionization constants for the amines were calculated from the hydrogen ion activities of the half-neutralized solutions by the equations

$$K_B{}_{CH_3OH} = \frac{1.95 \times 10^{-17}}{H \text{ ion activity}}$$

in the case of methanol and by the equation

$$K_B{}_{C_2H_5OH} = \frac{7.28 \times 10^{-20}}{H \text{ ion activity}}$$

in ethanol solutions. The value 1.9×10^{-17} given by Buckley and Hartley (5) for the dissociation constant of methanol was taken since the standard electrode potentials were also from the work of these authors. The value given by Bjerrum, Unmack and Zechmeister (2), 1.07×10^{-17} and 0.9×10^{-17}, are in good agreement with this value. For the ethanol solutions, the value 7.28×10^{-20} given by Danner (8) was used to calculate the dissociation constants in ethanol. MacFarlane and Hartley (24) also give a value 19×10^{-20} which is in fair agreement.

A comparison of the values for p-toluidine, aniline and m-chloroacetic in Table V and for acetic and benzoic acids in Table VI indicates that the values obtained and calculated by the above procedure are in approximate agreement with the values obtained by Goldschmidt by conductimetric measurement of the degree of alcoholysis of the salts. The value calculated from the concentration cell measurements are usually lower than the values obtained by Goldschmidt.

Table V.

A Comparison of the Measured and Calculated Ionization
Constants for a Series of Organic Acids in Water,
Methanol and Ethanol

Acid	Value of x	-Log K_a in					
		Water		Methanol		Ethanol	
		Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
Acetic	-1.65	4.77	4.73	9.61	9.65[b] 9.34[a]	10.61	10.39[a]
Formic	-0.40	4.74	3.68			10.58	11.15
Phenylacetic	-0.20	4.73	4.26			10.57	10.34
p-Toluic	3.40	4.40	4.29	9.24	9.33[a]	10.24	10.40[a]
Benzoic	3.95	4.25	4.18	9.09	9.12[a]	10.09	10.20[a] 10.43
p-Bromobenzoic	4.90	3.94	3.46	8.78	8.74a	9.78	9.65[a]
m-Chlorobenzoic	5.10	3.84	3.82	8.68	8.57[a]	9.68	9.57[a]
m-Nitrobenzoic	5.74	3.47	3.50			9.31	9.17
p-Nitrobenzoic	5.90	3.36	3.40			9.20	9.13
Salicylic	6.30	3.02	2.99	7.86	7.88		
3,5-Dinitrobenzoic	6.65	2.74	2.82	7.58	7.44	8.58	8.09
o-Nitrobenzoic	7.20	2.10	2.19			7.94	8.63
2,4-Dinitrobenzoic	7.60	1.50	1.40	6.34	6.47	7.34	7.33
Dichlororacetic	7.65	1.39	1.28	6.23	6.33	7.23	7.28

The values indicated by (a) have been determined in this
laboratory, the value indicated by (b) is reported by Bjerrum
(2); all other values are from the work of Goldschmidt (13)(14)
(15). The value of x for the electron sharing ability of the
radical was determined graphically.

Table VI.

A Comparison of the Measured and Calculated Ionization Constants of a Series of Primary Amines in Water, Methanol and Ethanol

Base	Value of x	-Log K_a in					
		Water		Methanol		Ethanol	
		Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
n-Butylamine	-1.65	3.40	3.39	4.88	4.92[a]	7.38	7.40[a]
Ammonia	-0.40	4.60	4.74	6.08	5.92[b]	8.58	8.66
o-Chlorobenzylamine	0.15	5.15	5.20[c]	6.62	6.61[a]	9.12	9.18[a]
p-Toluidine	3.40	8.70	8.76	10.18	10.00[a] 10.02	12.68	12.42[a] 12.91
m-Toluidine	3.85	9.24	9.20	10.72	10.80	13.22	13.24
Aniline	3.95	9.36	9.30	10.84	10.53[a] 10.70	13.34	12.95[a] 13.44
o-Toluidine	4.05	9.48	9.50	10.96	10.80	13.46	13.54
α-Naphthylamine	4.25	9.74	9.72	11.22	11.20	13.72	14.84
β-Naphthylamine	4.45	9.98	10.03	11.46	11.40	13.96	14.04
p-Chloroaniline	4.65	10.24	10.00	11.72	11.80	14.12	14.44
p-Bromoaniline	4.90	10.54	10.06	12.02	11.90	14.42	14.64
m-Chloroaniline	5.10	10.80	10.40	12.28	12.14[a] 12.30	14.78	14.80[a] 14.94
m-Bromoaniline	5.10	10.80	10.42	12.28	12.30	14.78	14.94
o-Chloroaniline	5.90	11.86	12.05	13.34	13.15	15.84	15.84
o-Bromoaniline	5.95	11.92		13.40	13.30	15.90	16.04

The values indicated by (a) have been determined in this laboratory; the value indicated by (b) has been reported both by Bjerrum (2) and Goldschmidt (14); the value indicated by (c) has been determined by Ware (28); all other values are from the work of Goldschmidt (13)(14)(15).

Suggestion of Equations to Correlate Experimental Results.

A graphical presentation of the data of Tables I and III is given in Figure 3. The data for the amines in Tables II and IV are presented in Figure 4. The curves for the amines have been drawn from the equations

$$+\log K_{B_{H_2O}} = y = -20e^{0.05x} + 15 \tag{1}$$

$$+\log K_{B_{CH_3OH}} = y = -20e^{0.05x} + 13.52 \tag{2}$$

$$+\log K_{B_{C_2H_5OH}} = y = -20e^{0.05x} + 11.02 \tag{3}$$

The equations for the acids curves are

$$+\log K_{a_{H_2O}} = y = 20e^{0.5x - 5.6} - 4.8 \tag{4}$$

$$+\log K_{a_{CH_3OH}} = y = 20e^{0.5x - 5.6} - 9.64 \tag{5}$$

$$+\log K_{a_{C_2H_5OH}} = y = 20e^{0.5x - 5.6} - 10.64 \tag{6}$$

Equations 1 and 4 for water solutions are those previously proposed by Johns and Hixon [20]. Equations 2 and 3 are easily obtained from Equation 1 by changing the final constant by the average difference between the value of the dissociation constant in water and in methyl or ethyl alcohol as the case may be. Also, the constants in equations 5 and 6 are changed by the average differences of the dissociation constants of the acids in water and either methyl or ethyl alcohol. This constant merely determines the position of the curve above the x axis and does not alter its slope or shape, which is to be expected from Brønsted's [3] generalization.

Fig. 3.

Electron sharing ability of organic radicals. (Acids)
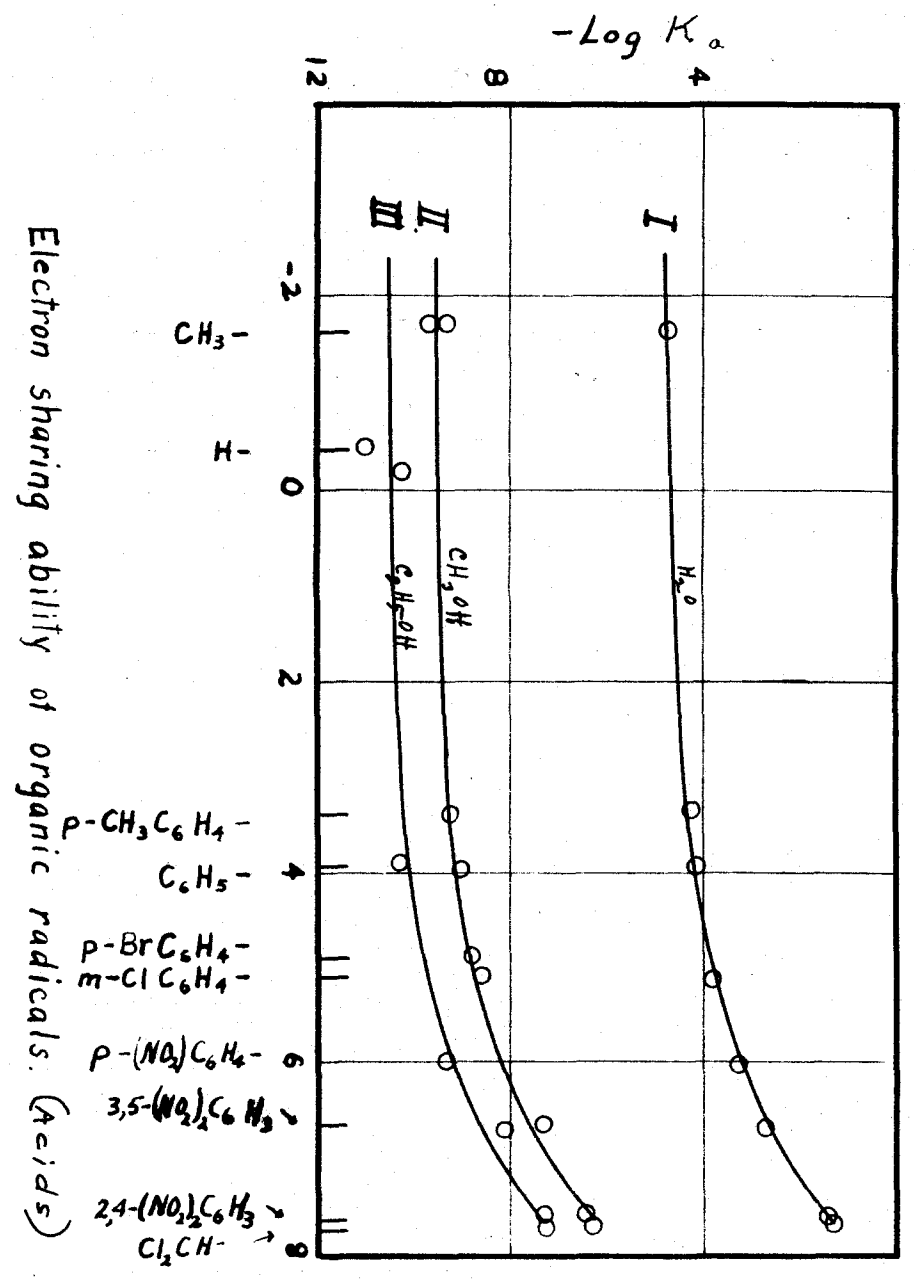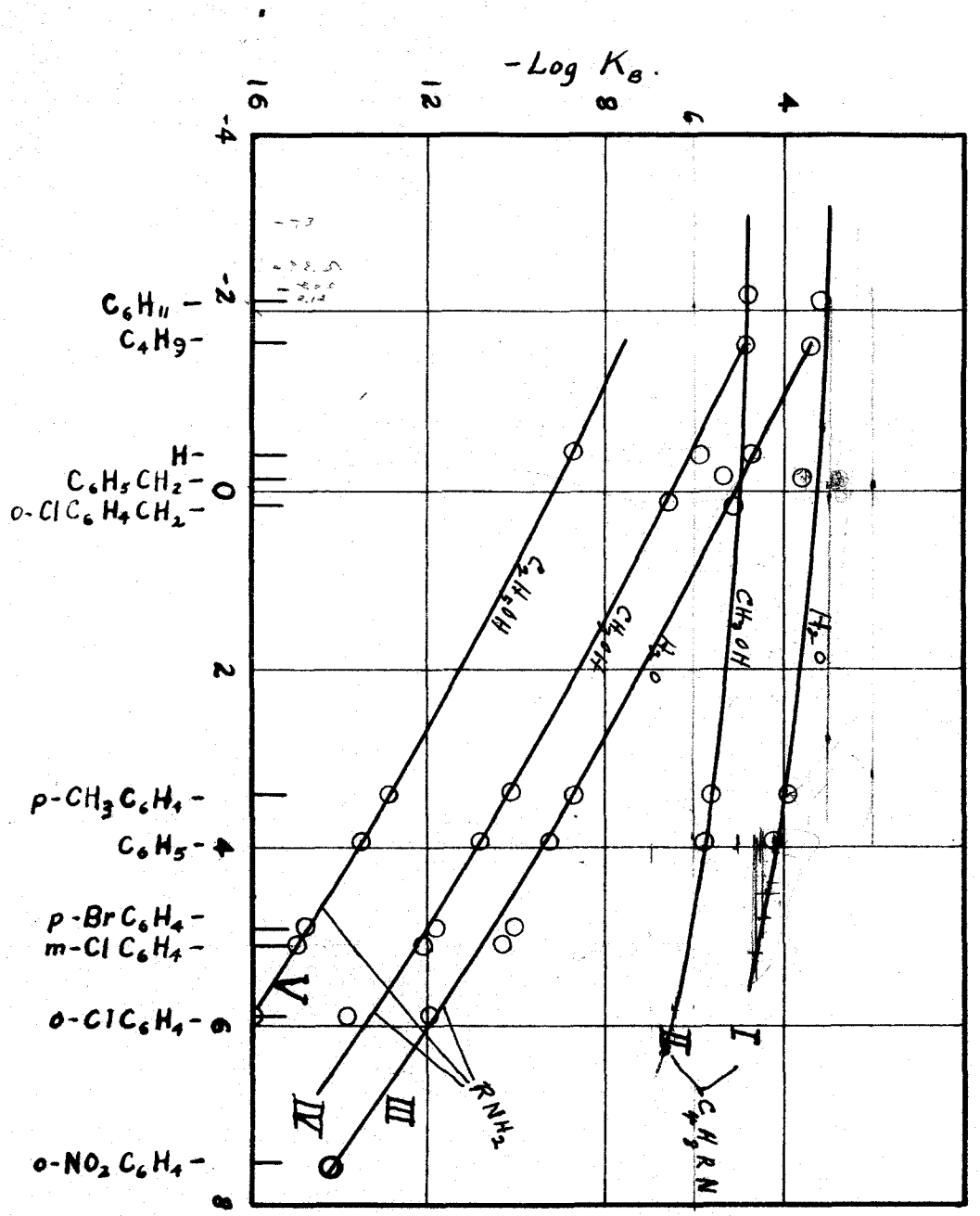
Electron sharing ability of organic radicals

Fig. 4.

The agreement between the measured values and the values calculated by the above equations can be seen in Tables V and VI. The irregularity in the case of formic acid was noted in the first paper (20) and attention should be called to the fact that this irregularity is less in the case of the ethanol measurement than in the case of the water measurement. The greatest deviations are to be found in the values reported by Goldschmidt for the acids in ethanol solution. It should be noted that this irregularity for the ethanol solutions does not hold for his measurements of the amines in the same solvent, all of the amine values being in substantial agreement with the calculated values. With the exception of formic acid, these deviations would appear to be associated with the less soluble compounds and are probably due to the deviations characteristic of saturated solutions. This point can be checked only as additional data are made available.

The ionization constants in methanol of the α-substituted pyrrolidines have been plotted in Figure 4 to show that they also have a similar relationship to the corresponding values in water (7)(27).

SUMMARY

1. The ionization constants of acetic, p-toluic, benzoic, p-bromobenzoic and m-chlorobenzoic acids; of n-butylamine, o-chlorobenzylamine, p-toluidine, aniline, and m-chloroaniline have been measured in both methanol and ethanol. Also, the α-cyclohexyl-, α-benzyl-, α-(p-tolyl), and α-phenyl pyrrolidines in methanol solutions have been measured using concentration cell methods analogous to the common procedure for water solutions.

2. The experimental difficulties in the measurement of the E.M.F. of alcoholic solutions due to the high internal resistance of the cells can be eliminated by the use of the vacuum tube potentiometer arrangement devised for measurements with the glass electrode in water solutions.

3. The value of new reference electrodes has been determined in both methyl and ethyl alcohol. The half cell employed was of the type

$$Hg/HgI_2(m_1) \ KI(m_2) \ //.$$
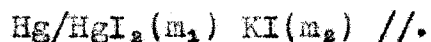
4. The ionization constants of the organic acids (R-COOH), of the primary amines (R-NH$_2$), and of the α-substituted pyrrolidines (R- $\underset{N}{}$) can be expressed as a mathematical function of the electron sharing ability of the variable organic radical (R) in the three solvents water, methanol and ethanol.

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