

over a concentration range of 0.003 to 0.025 molal. Their solutions contained also potassium oxalate and potassium acid oxalate so that it is not possible to calculate a standard e. m. f. from their data without certain assumptions concerning the activity coefficients of the ions involved. It is interesting to note that these authors obtained values for the *activity product* of cadmium oxalate which vary with the ionic strength. Since the method of calculation used by them appears to be entirely reasonable, it seemed likely to us that they had made an unfortunate choice of activity coefficients for use in equation (5) of their paper. It seems unlikely that the activity coefficient for undissociated oxalic acid could vary appreciably at the ionic strengths they used. We have recalculated values of the logarithm of the activity product of cadmium oxalate from their data, and by their method, but using different activity coefficients for the ions concerned.

According to the Debye-Hückel limiting law, the mean activity coefficient for a 1-2 electrolyte is equal to the square of the mean activity coefficient for a 1-1 electrolyte at the same ionic strength. Instead of the activity coefficients of Randall and Scott⁸ for sodium sulfate we have used the square of the activity coefficients for HCl, taken from Harned and Ehlers.⁹ We also used the more recent value of Harned and Fallon³ for K_2 for oxalic acid. These recalculations lead

(8) Randall and Scott, *THIS JOURNAL*, **49**, 654 (1927).

(9) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

to a value of the logarithm of the activity product, $\log_{10} K$, of -7.785 ± 0.005 , which shows no trend with changes in ionic strength.

Since the activity product of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ is a constant, we can obtain a constant value for the standard e. m. f. of the $\text{Cd}(\text{Hg}) \mid \text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}(\text{s}), \text{C}_2\text{O}_4^{2-}$ electrode since $E_{\text{Cd}/\text{CdC}_2\text{O}_4}^0 = E_{\text{Cd}/\text{Cd}^{++}} - 0.02957 \log_{10} K$. Again, since this standard e. m. f. is constant over a range of ionic strengths from 0.025 to 0.33, it appears that these changes in ionic strength do not produce any variation in the activity coefficient of un-ionized oxalic acid over the same range.

Summary

1. From measurements of the cell $\text{Hg} \mid \text{Hg}_2\text{C}_2\text{O}_4(\text{s}), \text{H}_2\text{C}_2\text{O}_4(c) \mid \text{H}_2$, we find the standard e. m. f. of the $\text{Hg} \mid \text{Hg}_2\text{C}_2\text{O}_4(\text{s}), \text{C}_2\text{O}_4^{2-}$ electrode to be -0.4173 ± 0.0001 v. These measurements also indicate that the activity coefficient of the undissociated oxalic acid does not change in value over an ionic strength range of 0.02 to 0.17.

2. Recalculation of the e. m. f. data of Clayton and Vosburgh⁷ for the cell $\text{Cd}(\text{Hg}) \mid \text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}(\text{s}), \text{H}_2\text{C}_2\text{O}_4(m), \text{quinhydrone} \mid (\text{Pt})$ indicates that the activity product of cadmium oxalate is a true constant over the ionic strength range from 0.025 to 0.33. This result leads to the conclusion that the activity coefficient of undissociated oxalic acid over the same ionic strength range does not change.

ST. PAUL, MINN.

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The Viscosity of Formamide-Dioxane Solutions at 5, 25 and 40°

By W. GEORGE PARKS,¹ I. MILTON LEBARON² AND EVERETT W. MOLLOY¹

Introduction

The viscosity of binary liquid solutions has been measured by several investigators³ in an attempt to correlate the viscosity with diverse physical properties such as migration of ions, conductivity, chemical constitution, association and hydration. In addition, attempts have been made to find mathematical expressions relating the viscosity of a solution to that of the components and their

ratio; also to deduce changes in a solution such as alterations in the degree of association, or the formation of complexes or compounds, from peculiarities in the viscosity-concentration curves.⁴ Any liquid or solution with marked anomalies from the point of view of one property is particularly desirable for such a study. Since pure formamide is an associated liquid⁵ with a high dielectric constant and 1,4-dioxane has a relatively low dielectric constant the viscosity-concentration curves for such a binary solution might show

(1) Rhode Island State College, Kingston, R. I.

(2) Present address, Colorado School of Mines, Golden, Colorado.

(3) Dunstan and Mussell, *J. Chem. Soc.*, **97**, 1935 (1910). Lemonde, *Ann. phys.*, **9**, 539 (1938). Merry and Turner, *J. Chem. Soc.*, **105**, 748 (1914).

(4) Spells, *Trans. Faraday Soc.*, **32**, 530 (1936).

(5) Turner and Merry, *J. Chem. Soc.*, **97**, 2069 (1910). Walden, *Z. physik. Chem.*, **75**, 555 (1910).

decided irregularities when compared with the data for solutions of water, acetic acid, and ethyl alcohol with formamide already reported in the literature. Furthermore, formamide-dioxane solutions are of considerable importance in investigating the properties of electrolytes in non-aqueous solutions because of the wide range in dielectric constant that can be obtained. It is necessary to know the variation of viscosity and density with composition of the solution. This investigation was undertaken in order to make available this information.

Experimental

Formamide.—The products of decomposition and hydrolysis were removed from the formamide by fractional distillation under reduced pressure. The formamide (99% m. p. -3 to -1°) after standing for several days over anhydrous sodium sulfate was twice distilled at 0.5 mm. pressure.⁶ The first and final 50 ml. of liquid were discarded each time. The final distillate was collected in a storage flask with suitable protection from moisture and air; m. p. 2.26° , d_{25}^{25} , 1.1302.⁷ According to the experiments of Eigenberger⁸ when acetaldehyde and methylene acetal are absent autoxidation does not occur.

1,4-Dioxane.—The dioxane (m. p. $10.5-11^\circ$) was purified by a modification of the method of Vingee.⁹ The liquid was refluxed for several hours with metallic sodium, fresh metal was added several times, and then distilled under atmospheric pressure (b. p. 101.4°). The middle fraction (approximately 75% of the total volume) was recrystallized three times by freezing. Approximately two-thirds of the liquid was crystallized each time. The final product was stored over metallic sodium in a protected flask; m. p. 11.6° , d_{25}^{25} , 1.0273.

Trimethylene Formal.—The trimethylene formal (1,3-dioxane) was secured from the Eastman Kodak Company and was not further purified; b. p. 106° at 760 mm. pressure.¹⁰

The viscosity measurements were made at 5, 25 and 40° using the master viscometer developed by Cannon and Fenske¹¹ (length of capillary 41.90 cm., volume of bulb 14.15 cc.). The calibration was checked periodically with pure water. Possible errors due to loading, drainage, alignment, surface tension and kinetic energy losses were carefully considered and corrections applied where necessary. The constant temperature oil-bath was equipped with a heating unit and cooling coils through which refrigerated calcium chloride brine was circulated. With adequate stirring and sensitive thermoionic relay control the desired temperatures were maintained to $\pm 0.02^\circ$. The viscometer was cleaned with dichromate cleaning solution and 5:1 hot nitric acid. Immediately before use it was

rinsed successively with distilled water, alcohol and ether. A current of clean dry air was passed through the instrument for five minutes. Since all binary liquid solutions were measured as rapidly as possible at the same temperature and the density was determined immediately after the measurement of viscosity it was not necessary to clean the instrument between measurements except at 5° . However, at the beginning of each series of measurements, that is, before either pure liquid was introduced, the instrument was thoroughly cleaned. This procedure eliminated the possibility of introducing any water or other foreign material. The solutions were prepared by volume and the weight per cent. calculated from the densities of the pure liquids. The apparatus was cleaned before each measurement at 5° because the density of liquid 1,4-dioxane cannot be determined at this temperature. The weight per cent. composition of the solutions at 25 and 5° was identical. In each case the viscometer was charged with a measured volume (30.0 ml.) of solution. Twenty to thirty minutes were allowed for thermal equilibrium to be attained before measurements were attempted. During this period the liquid was pulled into the upper bulbs several times by applying suction to the end of the capillary tube and allowed to run out again. This procedure insured adequate mixing and provided uniform temperature distribution. The time of efflux was measured to ± 0.1 sec. by means of a high-grade stop watch.

Experimental Results and Discussion

The experimental values of the viscosity at 5, 25 and 40° are summarized in Table I for different solutions of formamide and 1,4-dioxane. The viscosity (column 4) is expressed in centipoises. In each case the value reported represents the average of at least three separate determinations. A correction for the loss in kinetic energy was not necessary on account of the low velocities involved. No values are reported at 5° for either pure 1,4-dioxane or the 85.07% solution because crystals of dioxane separated at this temperature. The density reported in column 3 was determined by a pycnometer (25 ml. capacity) at 25 and 40° . The Westphal balance was used at 5° . In Table II the experimental data for various solutions of formamide and 1,3-dioxane are given.

The density and viscosity at 25° of pure formamide are in excellent agreement with the data recorded by Smith⁷ and by English and Turner.¹² They found the density and viscosity to be 1.1292–1.1307 and 3.302, respectively. The results for pure 1,4-dioxane are slightly lower than those of Geddes¹³ who found the viscosity to be 1.1969 and 0.9415 at 25 and 40° , respectively.

The density of the binary liquid solutions is plotted against the weight per cent. formamide in

(6) Magill, *Ind. Eng. Chem.*, **26**, 611 (1934).

(7) Brann, *THIS JOURNAL*, **40**, 793 (1918); Smith, *J. Chem. Soc.*, 3257 (1931).

(8) Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).

(9) Vingee, *THIS JOURNAL*, **56**, 513 (1934).

(10) Birchall and Coffey, British Patent 338,624 (Aug. 30, 1929); Clarke, *J. Chem. Soc.*, **101**, 1803 (1912).

(11) Cannon and Fenske, *Oil and Gas J.*, **34**, 45 (1936).

(12) English and Turner, *J. Chem. Soc.* **105**, 1656 (1914).

(13) Geddes, *THIS JOURNAL*, **55**, 4832 (1933).

TABLE I

VISCOSITY OF FORMAMIDE-1,4-DIOXANE SOLUTIONS			
Weight % formamide	Time, sec.	Density	Viscosity (centipoises)
5°			
100.00	780.8	1.146	5.9785
93.24	799.2	1.137	6.0729
85.81	796.0	1.129	6.0061
77.90	773.2	1.120	5.7883
69.35	735.4	1.112	5.4661
60.04	668.3	1.102	4.9220
50.45	585.8	1.093	4.2786
39.44	493.4	1.081	3.5642
28.08	400.6	1.072	2.8697
14.93
0.00
25°			
100.00	437.5	1.1302	3.3039
93.24	448.2	1.1226	3.3629
85.81	451.3	1.1144	3.3613
77.90	441.4	1.1053	3.2603
69.35	422.2	1.0965	3.0936
60.04	394.2	1.0867	2.8625
50.45	356.3	1.0767	2.5636
39.44	311.6	1.0655	2.2190
28.08	262.5	1.0542	1.8490
14.93	214.4	1.0414	1.4920
0.00	174.0	1.0273	1.1951
40°			
100.00	313.9	1.1126	2.3345
93.15	320.0	1.1044	2.3616
85.91	319.3	1.0959	2.3376
78.55	315.6	1.0874	2.2940
70.56	304.4	1.0783	2.1934
61.60	285.7	1.0680	2.0390
51.98	261.2	1.0578	1.8463
41.38	231.9	1.0464	1.6215
30.10	200.1	1.0346	1.3827
15.87	167.0	1.0200	1.1383
0.00	139.1	1.0042	0.9341

TABLE II

VISCOSITY OF FORMAMIDE-1,3-DIOXANE SOLUTIONS			
Weight % formamide	Time, sec.	Density	Viscosity (centipoises)
5°			
100.00	780.9	1.146	5.9785
91.65	795.7	1.135	6.0531
76.73	726.2	1.118	5.4261
43.52	449.4	1.081	3.2470
0.00
25°			
100.00	437.5	1.1302	3.3039
91.65	439.3	1.1207	3.3277
76.73	423.4	1.1025	3.1193
43.52	286.4	1.0651	2.0391
0.00	154.0	1.0269	1.0567
40°			
100.00	313.9	1.1126	2.3345
91.60	321.1	1.1026	2.3656
77.21	302.8	1.0852	2.1959
45.02	225.7	1.0485	1.5813
0.00	126.1	1.0039	0.8452

variation in density of pure formamide and 1,4-dioxane with temperature is expressed by

$$d = \frac{T}{0.902T - 0.18} \tag{4}$$

$$d = \frac{T}{0.990T - 0.15} \tag{5}$$

where T represents the absolute temperature and d the density of pure formamide (Equation 4) and 1,4-dioxane (Equation 5). The maximum error is 0.5%.

Fig. 1. The volume change on mixing the two associated liquids is negligible as shown by a plot of per cent. composition by volume against density or specific volume. On this basis we are permitted to calculate the composition of the solutions directly from the density measurements.

The relationship between the density and composition is expressed by the equations

$$d_{40^\circ} = 1.0042e^{0.10316P} \tag{1}$$

$$d_{25^\circ} = 1.0273e^{0.09476P} \tag{2}$$

$$d_{5^\circ} = 1.0429e^{0.09281P} \tag{3}$$

with a maximum error of $\pm 0.05\%$. P represents an abscissa on the density-composition curve (Fig. 1) expressed in decimal form ($\%/100$). Over the temperature interval investigated the

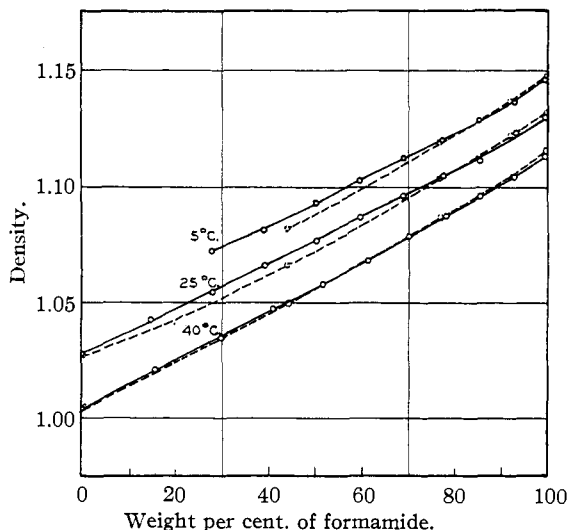


Fig. 1.—Density of formamide: — 1,4-dioxane solutions; ---- 1,3-dioxane solutions.

The viscosity of the solutions is plotted against the composition by weight in Fig. 2. The curves

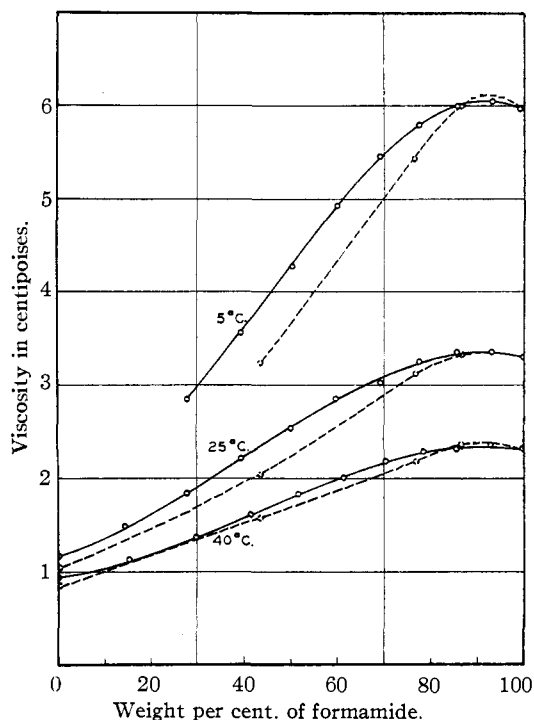


Fig. 2.—Viscosity of formamide: — 1,4-dioxane solutions; --- 1,3-dioxane solutions.

indicate that association decreases with increase in temperature as expected. Due to the unusual form of the curves considerable difficulty was experienced in attempting to obtain a mathematical expression for the relationship between viscosity and composition. The substitution of fluidity for viscosity was of no advantage in this case. The viscosity at 5°, from 50–100 weight per cent. formamide, may be expressed by the equation

$$\eta_5 = 0.7465 + 0.072X - 1.968 \times 10^{-10}X^5 \quad (6)$$

where X is the composition of the binary solution in weight per cent. The maximum error is $\pm 0.5\%$. However, between 75–100 weight per cent. formamide the maximum error is only $\pm 0.03\%$. At 25° between 0–50 weight per cent. formamide

$$\eta_{25} = 1.1951e^{0.01554X} \quad (7)$$

The maximum error is $\pm 0.03\%$. Between 50–100 weight per cent. equation (7) becomes

$$\eta_{25} = 1.1951e^{0.01554X} + 0.159 - 2.493 \times 10^{-8}X^4 \quad (8)$$

The maximum error is $\pm 0.3\%$. At 40° between 50–100 weight per cent. formamide

$$\eta_{40} = 0.6165 + 0.025X - 7.786 \times 10^{-9}X^4 \quad (9)$$

The maximum error is $\pm 0.3\%$ for 50 weight per cent. formamide.

A number of empirical formulas¹⁴ have been developed to represent the variation of viscosity with concentration but only a few make any claim to generality, while none, so far as is known to the authors, will fit the curves of the type obtained with solutions of 1,4-dioxane and formamide. The complicated nature of the problem requires the introduction of a number of arbitrary assumptions (free space, "binary viscosity," association, specific volume, etc.) whenever the treatment applied to pure liquids is extended to liquid solutions.

The viscosity of a homogeneous binary liquid solution is not a linear function of the composition as has been assumed by some investigators. The curves are usually sagged with a definite maximum or minimum. The ratio at which the maximum occurs is a function of the temperature, and shifts with increase in temperature toward the viscosity of the more viscous component. Very high maxima occur with mixtures of several organic liquids such as the alcohols and acetic acid with water.¹⁵ The curves flatten rapidly with rising temperature. The maxima are believed to occur whenever there is chemical combination forming compounds or definite solvates. A possible criterion of combination should be that the position of the maximum be invariant with temperature. Dunstan and Mussell³ believe that an increase in viscosity with increasing amide concentration indicates association. Solutions showing viscosity maxima may also show definite contraction. According to Fig. 2 the maximum (greatest deviation from linearity) in each curve occurs at approximately 91 weight per cent. formamide. This indicates a compound ratio of 5 molecules of formamide to 1 of dioxane ($C_4H_8O_2 \cdot 5HCONH_2$). This compound is of the same type as that found by Geddes¹³ in solutions of dioxane in water. Viscosity data alone are not sufficient to establish the existence of the compound. Isolation and analysis are the only satisfactory tests. The viscosity-concentration curves in Fig. 2 are quite similar to those obtained for solutions of *m*-cresol with aniline and with *o*-toluidine when one molecule of each substance combines to form a definite compound. Solutions of pyridine and acetic acid have a much more pronounced maximum.

English and Turner¹² found that formamide

(14) Ishikawa, *Bull. Chem. Soc. Japan*, **11**, 64 (1936); McLeod, *Trans. Faraday Soc.*, **19**, 17 (1923); **30**, 482 (1934); Spills, *ibid.*, **32**, 530 (1936).

(15) Bingham and Jackson, *U. S. Bur. Standards Bull.*, 298 (1917).

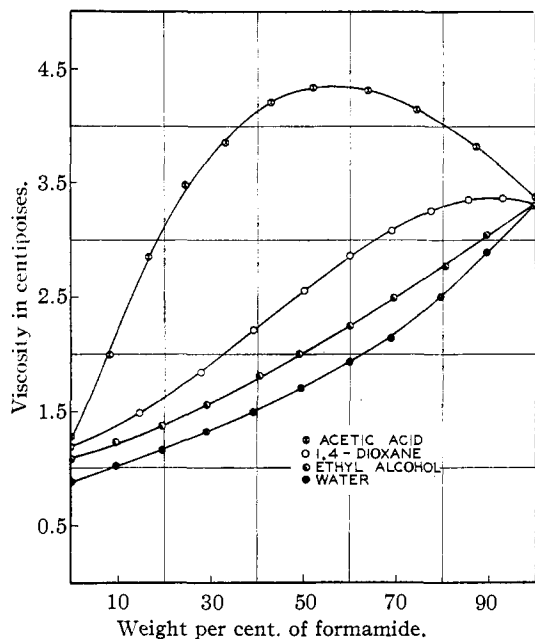


Fig. 3.—The viscosities of some binary liquid mixtures containing formamide at 25°.

forms solutions of maximum viscosity with aliphatic acids except formic. However, there was no evidence of chemical combination (maxima) by formamide with water and the lower alcohols³ at 25 and 40°. The curves are shown in Fig. 3 for comparison. The viscosity of formamide in 1,4-dioxane is higher than that in water and ethyl alcohol which indicates a greater degree of association. Formamide is more easily dissociated in water. The association effect is much greater in acetic acid solution as shown by the curves. However, molecular symmetry cannot be ignored when making such comparisons.

When viscosity is plotted against concentration (Fig. 2) if a contraction in volume occurs the curves are sagged, that is, the viscosity at any given concentration is less than the value which would be given by a linear law. A minimum is indicated at the higher temperatures (Fig. 2) at approximately 20 weight per cent. formamide. In the case of the density (Fig. 1) this means that an expansion takes place on mixing the two components. When a liquid expands due to the release of a compression a decrease in the viscosity occurs. The absence of a volume change on mixing may indicate a linear law but is not necessarily the only criterion for a perfect solution. There is no theoretical justification for the viscosity-concentration linear law for binary liquid solutions. The curve is not known for an ideal solution.

The results are recorded for three temperatures because although there appears to be no simple relation between molecular polarization and viscosity Andrade¹⁶ has indicated that an investigation of the rate of change of viscosity of liquids with temperature may eventually supply information of a fundamental nature.

A nomograph showing the relationship between temperature and viscosity for formamide-1,4-dioxane solutions is given in Fig. 4. The curve indicates weight per cent. formamide. The maximum error is 1%.

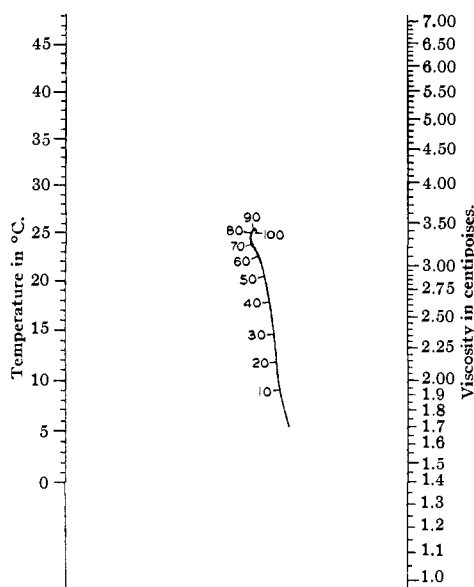


Fig. 4.—Nomograph of formamide-1,4-dioxane solutions.

For comparison measurements were made with 1,3-dioxane. The data are recorded in Table II and shown on Figs. 1 and 2. The investigation was not extended because no significant differences were observed when the *m*-dioxane was substituted for *p*-dioxane.

Summary

1. The viscosity and density of formamide-1,4-dioxane solutions has been measured at 5, 25 and 40° from 0-100 weight per cent. formamide. The data are compared with those of acetic acid, ethyl alcohol and water in formamide solutions.
2. The variation of the density of pure formamide and pure 1,4-dioxane with temperature, the relationship between density and composition, also viscosity and composition are expressed by mathematical equations.
3. The viscosity-concentration curves show

(16) Andrade, *Phil. Mag.*, 17, 497 (1934).

an increase in viscosity with increasing concentration of formamide from 20 to 91 weight per cent. The viscosity then decreases to the value of pure formamide.

4. The results indicate a negligible change in

volume on mixing the two associated liquids.

5. The formation of the compound $C_6H_5O_2 \cdot 5HCONH_2$ is indicated by the maximum in the viscosity curves.

KINGSTON, RHODE ISLAND

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The Electron-Sharing Ability of Organic Radicals. XIV. The Effect of the Radicals on the Ionizing Power of Organic Solvents

BY FRANK J. MOORE AND I. B. JOHNS

In a general way the greater the dielectric constant of a solvent the greater is its ionizing power. This fact was observed independently by Nernst and by Thomson and has been formulated into the rule which bears their names. The fact that other effects beside that of the dielectric constant must be considered in accounting for ionizing power has been recognized by many experimenters.

The factors determining the degree of ionization of weak acids have been summarized by Wynne-Jones.¹ They are three. First, the electrostatic action between the solvated proton and the acid ion depends in part upon the dielectric constant of the solvent. Second, the chemical potentials of the solvated proton and the acid ion may vary with the solvent. Though this variation is difficult to estimate, Wynne-Jones concludes, in agreement with Bjerrum and Larsson,² that the chemical potentials of the two ions should undergo the same variation with change of solvent. Third, the basicities or proton accepting powers of the various solvents are different. This factor is the subject of the present paper.

The measurement of the basicities of the various solvents is complicated by several difficulties. First, in order that the solute be not an ion aggregate and hence subject to treatment of the type which Debye and Hückel have given, one is limited to the weak acids. Thus one is forced to make measurements on weak electrolytes in solvents possessing much less ionizing power than does water. In the present work picric acid was the solute chosen.

The second complication arises from the fact that once ionization takes place the attractions

between the ions will depend upon the dielectric constant of the solvent. This effect will, of course, be included in the ionization constants which are used for comparing the ionizing powers of the solvents. Accordingly in the present study solvents having nearly identical dielectric constants were used.

Finally, a suitable scale is needed for measuring the electronic properties of the radicals attached to the polar group of the solvent molecule. In earlier papers in this series³ such a scale has been given. The radicals are arranged in the order of their effect on the ionization constant of the carboxyl group. Since the constants were determined in one solvent for any given series of acids it is certain that the scale by which the radicals are compared is free from any effect of dielectric constants.

A later paper⁴ has shown that the normalizing power of a series of ketones depends in a regular way on this electron-sharing ability of the radicals attached to the carbonyl group. From this one may conclude that the attraction of the solvent molecule for the proton is a function of the electron-sharing ability of the radicals attached to the polar group. As the electron-sharing ability of the radical increases the donor power of the functional group decreases with a corresponding weakening of the proton-solvent bond resulting in decreased ionization.

Ketones and nitriles were chosen as solvents in the present work because their functional groups have neither so high nor so low an inherent basicity that variations due to the radicals should be too small for convenient measurement. Fur-

(1) W. F. K. Wynne-Jones, *Proc. Roy. Soc. (London)*, **A140**, 440 (1933).

(2) N. Bjerrum and E. Larsson, *Z. physik. Chem.*, **127**, 358 (1927).

(3) R. M. Hixon and I. B. Johns, *THIS JOURNAL*, **49**, 1786 (1927); L. D. Goodhue and R. M. Hixon, *ibid.*, **56**, 1329 (1934); **57**, 1688 (1935).

(4) F. A. Landee and I. B. Johns, *ibid.*, **63**, 2895 (1941).