

Discussion

How the presence and subsequent fermentation of a very small quantity of dextrose can hasten the fermentation of maltose is rather difficult to explain. One supposition involves a change in the permeability of the cell wall. This seems logical since, it may be recalled, a maltase-active extract can be made from a yeast which is slow to ferment maltose. Since maltase was present in the interior of the cell an increased permeability to the disaccharide maltose should produce a corresponding increase in fermentation rate.

The results we have here reported indicate that one might easily be misled in a search for fermentation activators of maltose fermentation. The seemingly dual nature of the accelerators, one heat labile and one heat stable, as well as the known influence of thiamin, produces a rather complex system. The action of maltase upon maltose fermentation is obvious and there is no reason to consider maltase a fermentation activator or accelerator according to the present usage of these terms. On the other hand, the

action of dextrose may be considered to activate a fermentation system contained in the cell.

Summary

Dried yeast prepared from baker's yeast contains maltase and the addition of such dried yeast or an extract made from it to a yeast-maltose system will cause a sharp increase in the initial rate of fermentation.

Small quantities of dextrose when added to a yeast-maltose system greatly hasten the appearance of active fermentation.

The influence of small quantities of dextrose may be used to estimate dextrose when present as a minor constituent of maltose preparations.

The initial rate of fermentation of maltose is dependent upon the pH and shows an optimum in the region of pH 4.5.

Small quantities of maltase and dextrose, either separately or together, may be responsible for some of the action of the various accelerators of maltose fermentation.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Conductance of Some Salts in Tricresyl Phosphate at 40°

BY MYRON A. ELLIOTT WITH RAYMOND M. FUOSS

I. Introduction

A large number of electrolytic systems in non-aqueous solvents have been studied, but data are lacking on systems where the solvent molecules are large compared to those of the solute. Furthermore, a systematic general study of temperature coefficients is not yet available. Experimental data on these problems are necessary for a clear understanding of the dynamics of electrolytic conductance; Stokes' law, as applied in the form of Walden's rule is, at best, a first approximation. In this paper will be presented the results of a study of a group of electrolytes in tricresyl phosphate $[(\text{CH}_3\text{C}_6\text{H}_4\text{O})_3\text{PO}]$ at 40°. This solvent has a high viscosity at room temperatures, with a large temperature-viscosity coefficient, and a fairly low dielectric constant (6.92 at 40° and 60 cycles). These properties make it a very useful solvent medium for an experimental investigation of the problems under consideration.

Some aromatic amine picrates were included among the salts studied; they all gave unusual conductance curves in that the shape of the conductance-concentration curve was that of a curve for a strong electrolyte, while the magnitude of the conductance was that of a very weak electrolyte. This result suggests that two modifications of amine picrates exist, a non-electrolytic molecular addition compound, and an electrolytic compound which is a true salt, formed by the migration of a proton from the picric acid to the amine, to form an ammonium salt.

II. Materials, Apparatus and Method

Tricresyl phosphate was purified by heating for two hours at 50°, with constant stirring, with previously dried fuller's earth (about 300 g. of adsorbent to 2.5 l. of solvent). After pumping the dissolved air out of the hot tricresyl phosphate, it was filtered to remove the fuller's earth. The following procedure was used. The degassed mixture of fuller's earth and tricresyl phosphate was allowed to settle overnight in a long vertical tube 10 cm. in diameter, containing an inverted sintered glass funnel attached

to an outlet leading to a collection flask. After settling, the liquid was drawn by vacuum through the filter into the flask; the first portion was turbid and was therefore discarded, but after a filter mat of fuller's earth had been deposited on the sintered disk, the filtrate became clear. The tricresyl phosphate was stored in bottles equipped with drying tubes, from which it was pumped by dry air pressure into the conductance cells or dilution flasks. The conductance of the dried solvent at 40° was of the order of 2×10^{-11} mho; the best value was 0.5×10^{-11} .

The viscosity of the tricresyl phosphate was determined in a Saybold Universal viscometer by the Schenectady Works Laboratory. The results are given in Table I. The logarithm of viscosity plotted against the reciprocal of the absolute temperature gives a straight line, with a slope corresponding to a molar "heat of activation" of nearly 10 kcal. The density of our tricresyl phosphate at 40.00° is 1.1527, as determined by pycnometer weighings. (Densities of different lots vary slightly, with varying isomer proportions.)

, °C.	Saybold	η
35	155 sec.	0.388
45	98	0.231
55	69	0.145

Salts.—Tetrabutylammonium picrate was very kindly given to us by Dr. Charles A. Kraus of Brown University. Lead abietate was that prepared by Dr. V. Deitz in connection with work on another problem in this Laboratory.¹ The amine picrates were prepared by mixing hot alcoholic solutions of equivalent amounts of the corresponding amine and of picric acid. They were then recrystallized from alcohol, water, or mixtures of these solvents: tributylammonium picrate, m. p. 106.9°; tribenzylammonium picrate, m. p. 191°; aniline picrate, dec. 175–177°; dimethylaniline picrate, m. p. 159°; *p*-phenylaniline picrate, dec. 205–207°.

Conductance Cells.—Part of the conductance measurements were made in the dilution cell used by Deitz and Fuoss.¹ Others were made in a guarded cell which consisted of concentric cylindrical electrodes mounted on a fired soapstone separator; the electrodes formed the cell walls (see Fig. 1). The cell constant was equal to 0.002720; it was reproducible to $\pm 0.1\%$ on repeated reassembly of the cell. The surfaces in contact with the solution were gold plated. The electrodes were cleaned between runs by scrubbing with hot 20% caustic solution, followed by hot water, after which they were dried in an oven at 120°. The procedure in using this cell was as follows. A solution was made up in a flask, and then a portion was pipetted into the cell, taking precautions to avoid moisture. After coming to equilibrium in the oil thermostat (maintained at

40 \pm 0.01°), the cell was emptied, and a second portion of the same solution was added and measured. This procedure was repeated until the resistances of two successive fillings agreed to 0.2%. This procedure eliminates errors due to sorption difficulties, and permitted us to obtain reliable reproducible results at dilutions as great as ten million liters of solvent per mole of salt.²

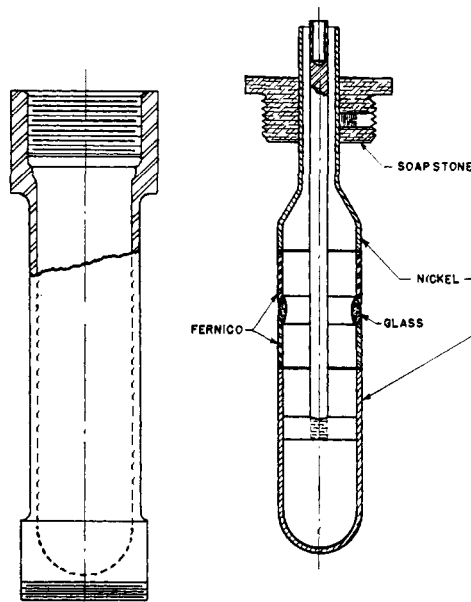


Fig. 1.—Guarded conductance cell for liquids.

The magnitude of the amount of salt adsorbed is rather interesting; in one experiment with the platinum electrodes, the cell was filled with a solution of tributylammonium picrate whose nominal concentration was $4.35 \times 10^{-7} N$. The specific conductance was 0.97×10^{-10} on the first filling, but rose on repeated fillings to 6.00×10^{-10} . The initial conductance corresponded to a concentration of about 0.52×10^{-7} ; in other words, 88% of the first portion of electrolyte was adsorbed. If we calculate, from the amount of solution added to the cell and the area of the electrodes, the average area occupied per ion which vanished from solution, we find 6.8×10^{-16} cm.² This figure corresponds to a monomolecular layer of ions adsorbed on the platinum. The actual amount adsorbed depends somewhat on the concentration of electrolyte in contact with the electrodes; the greatest change in apparent conductance always occurs between the first and second fillings of the cell, after which the changes are of second order (Ref. 2, Tables I and II).

(1) Deitz and Fuoss, *THIS JOURNAL*, **60**, 2394 (1938).

(2) Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

Electrical Equipment.—The Schering bridge and the resistance bridge, used for other work in this Laboratory,³ were used in determining the conductances. All of the present work is at 60 cycles.

Procedure.—Conductance runs were made by both dilution and concentration methods. All solutions were made up by weight; the density of the pure solvent was used in calculating normalities from the weight concentrations. This approximation is justified by the low total concentrations used.

III. Experimental Results

The conductance data are summarized in Table II, where concentrations in equivalents of salt per liter of solution at 40° and the corresponding equivalent conductances are given. In order to save space, the data are not separated into groups of figures for each run; however, at least two runs, each starting with independent salt weighings, were made for each salt, and when only two runs were made for a given salt, one was by the dilution method and the other by the concentration method.

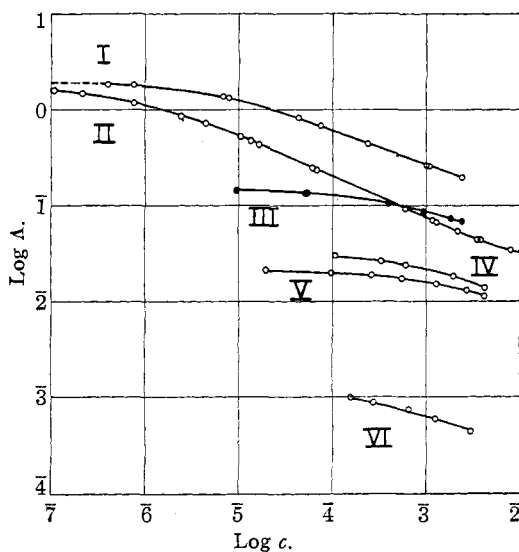


Fig. 2.—Conductance curves in tricresyl phosphate at 40°: I, Bu_4Npi ; II, Bu_3HNpi ; III, $\text{B}_2\text{H}_3\text{HNpi}$; IV, PhH_3Npi ; V, $\text{PhC}_6\text{H}_4\text{H}_3\text{Npi}$ and PhMe_2HNpi ; VI, PbAb_2 .

IV. Discussion of Results

In Fig. 2, the data of Table II are plotted on a log-log scale in order to facilitate qualitative comparison of the different compounds. (The points

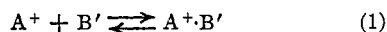
(3) FUOSS, THIS JOURNAL, **60**, 451 (1938).

TABLE II CONDUCTANCES OF SALTS IN TRICRESYL PHOSPHATE AT 40°			
Tributylammonium picrate		Tetrabutylammonium picrate	
c	Λ	c	Λ
0.01648	0.02904	0.002423	0.1937
.00799	.03366	.0 ₂ 1077	.2511
.003798	.04334	.0 ₂ 1001	.2569
.003584	.04380	.0 ₂ 2351	.4411
.002205	.05364	.0 ₇ 7454	.669
.001287	.0671	.0 ₄ 4298	.809
.001178	.0688	.0 ₆ 7798	1.321
.0 ₃ 6045	.0923	.0 ₆ 6793	1.359
.0 ₆ 599	.2340	.0 ₆ 7646	1.818
.0 ₆ 681	.2452	.0 ₆ 4016	1.831
.0 ₄ 1629	.4235		
.0 ₄ 1305	.4644		
.0 ₄ 1030	.5126		
.0 ₃ 4363	.717		
.0 ₆ 2386	.860		
.0 ₆ 7877	1.192		
.0 ₆ 7602	1.189		
.0 ₆ 2165	1.494		
.0 ₆ 1078	1.603		
Aniline picrate		Tribenzylammonium picrate	
0.004168	0.01462	0.002462	0.06766
.001950	.01804	.001842	.07215
.0 ₃ 6013	.02383	.0 ₃ 9301	.0864
.0 ₃ 3279	.02617	.0 ₃ 3867	.1059
.0 ₃ 1044	.02965	.0 ₅ 260	.1343
		.0 ₅ 043	.1338
		.0 ₆ 9493	.143
p-Phenylaniline picrate		Dimethylaniline picrate	
0.004123	0.01134	0.003598	0.01386
.002699	.01306	.002744	.01423
.001296	.01499	.0 ₅ 5478	.01800
.0 ₃ 5522	.01738	.0 ₅ 5207	.01780
.0 ₃ 2568	.01852	.0 ₃ 1331	.01954
.0 ₉ 463	.0193	.0 ₂ 2424	.02185
.0 ₄ 1916	.0216		
		Lead abietate	
		0.002947	0.0 ₄ 32
		.001231	.0 ₃ 592
		.0 ₃ 6529	.0 ₇ 748
		.0 ₃ 2718	.0 ₈ 878
		.0 ₃ 1553	.0 ₉ 981

for dimethylaniline picrate have been omitted for the sake of simplification; the conductance values for this salt are nearly identical with those for *p*-phenylaniline picrate.) The curves for Bu_4Npi and Bu_3HNpi are about what might be expected; the former is concave down over the entire concentration range studied, and below 10^{-5} normal begins rapidly to approach a limiting asymptote. The curve for the tributyl salt lies below that for the tetra salt over the finite concentration range, and begins to show an approach to its asymptote only at concentrations of the order of 10^{-7} normal. An inflection point appears near 10^{-4} normal, and it seems probable that a minimum in the conductance curve would appear above 0.01 normal. In other words, the tri salt shows more binary association at any given concentration than the tetra salt, and gives evidence of triple ion formation at higher concentrations, but both tend to approximately the

same value of limiting conductance at zero concentration. These facts could all have been predicted from the structure of the salts and the properties of the solvent.

A quantitative analysis of the data for these two salts permits evaluation of the limiting conductance Λ_0 and of the dissociation constant K for the binary equilibrium⁴



The corresponding $F/\Lambda - c\Lambda f^2/F$ plots are shown in Fig. 3. For Bu_4MPi , we obtain $\Lambda_0 = 1.95$ and $K = 1.014 \times 10^{-5}$; for Bu_3HNpi , $\Lambda_0 = 1.73$ and $K = 1.18 \times 10^{-6}$. For the triple ion equilibrium constant for Bu_3HNpi , obtained by plotting $\Lambda\sqrt{c}g(c)$ against $c(1 - \Lambda/\Lambda_0)$, we find $k_3 = 0.0393$. If we calculate the effective size of the equivalent spherical ions from K by suitable application of Coulomb's law,⁴ we find $a = 5.80 \times 10^{-8}$ cm. for the tetra salt, and $a = 4.66 \times 10^{-8}$ cm. for the tri salt. Aside from the fact that $\Lambda_0(Bu_4Npi) > \Lambda_0(Bu_3HNpi)$, which might be explained on the basis of interaction between the $-NH$ dipoles of the positive ions of the tri salt and the $\equiv PO$ dipoles of the solvent molecules, all of these figures are of the expected order of magnitude.

In ethylene chloride, Mead⁵ found $\Lambda_0(Bu_4Npi) = 57.40$ at 25.00° . We therefore have $\Lambda_0\eta = 0.4508$ for tetrabutylammonium picrate in ethylene chloride at 25° , using $\eta(C_2H_4Cl_2) = 0.007853$. For the same salt in tricresyl phosphate, we have $\Lambda_0\eta = (1.95)(0.295) = 0.575$. The ratio of the $\Lambda_0\eta$ products in the two solvents is 1.275 and differs from unity by much more than the estimated experimental error in any of the four data involved. We must therefore accept the fact that the ions of tetrabutylammonium picrate move nearly 30% faster in tricresyl phosphate than in ethylene chloride, under the same potential gradient, after correction for the difference in macroscopic viscosity is made by application of Stokes' law. As a tentative explanation, we suggest that the effectively greater mobility in tricresyl phosphate is due to slipping. In ethylene chloride, the solute ions are much larger than the solvent molecules, and the physical approximation that the solvent is a continuous medium is to some extent at least justified; in tricresyl phosphate, on the other hand, this approximation no longer seems permissible, because the solvent

molecules are now larger than the ions, and, for that reason, a modification of the simple hydrodynamics becomes necessary. The most obvious correction is to make allowance for the greater probability that a small ion can pass between certain configurations of large solvent molecules without displacing them, and this slipping will naturally lead to an effectively greater relative mobility.

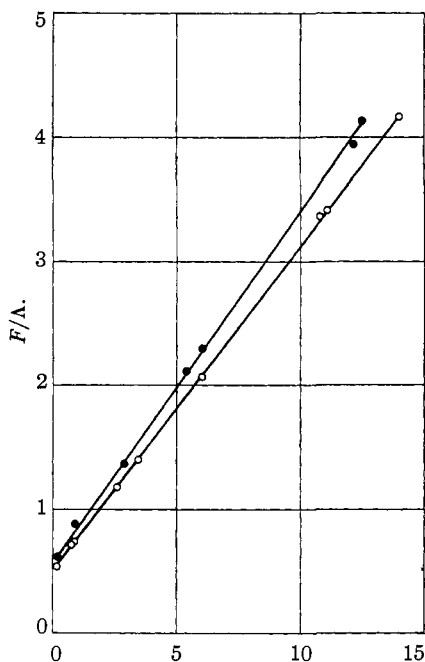


Fig. 3.—Extrapolation plots for: ●, Bu_3HNpi , abscissa = $(c\Lambda f^2/F) \times 10^6$; ○, Bu_4Npi , abscissa = $(c\Lambda f^2/F) \times 10^6$.

One other anomaly appears in the case of the tetrabutylammonium picrate. It has been shown that, in general, equations based on the binary equilibrium (1) should fail at concentrations greater than a critical concentration determined by the dielectric constant and temperature of the solvent.⁶ For tricresyl phosphate at 40° , this concentration is 1.2×10^{-4} ; yet the points of Fig. 3 lie on a straight line up to the highest concentration studied, which was 2.4×10^{-3} , or twenty times the limiting concentration. In all cases previously encountered, deviations from linearity on a $F/\Lambda - c\Lambda f^2/F$ plot have always appeared at the neighborhood of the critical concentration. We can only conclude that the dielectric constant is not the sole determining factor in controlling association. Again, it seems

(4) Fuoss, *Chem. Rev.*, **17**, 27 (1935).

(5) Mead, Kraus and Fuoss, *Trans. Faraday Soc.*, **32**, 594 (1936).

(6) Fuoss, *This Journal*, **57**, 2604 (1935).

probable that the representation of the solvent as a continuous medium is going to lead to electrical as well as to hydrodynamic difficulties. Further work, covering a wider range of molecular parameters, is emphatically needed.

We now turn to the last five salts of Table II. In Fig. 2, it will be seen that they all give much the same shape curves and, except for the lead abietate, they all closely resemble the 10^{-5} – 10^{-7} range of the curve for tetrabutylammonium picrate; *i. e.*, they are concave down, and appear to be approaching an asymptote. But the values of the asymptotes approached correspond to absurdly small values, if these asymptotic values are to be interpreted as limiting mobilities.

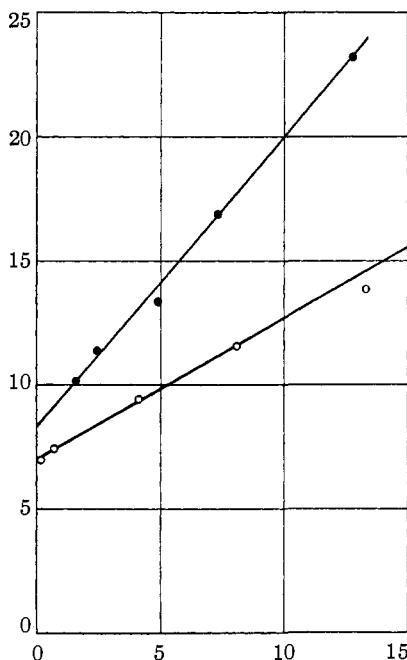
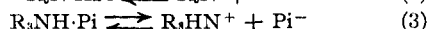
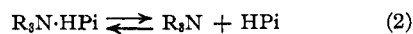


Fig. 4.—Extrapolation plots for: ● Pb-Ab₂, ordinate = $(1/\Lambda) \times 10^4$, abscissa = $(c\Lambda) \times 10^7$; ○ Bz₂HNPI, ordinate = $1/\Lambda$, abscissa = $(c\Lambda) \times 10^6$.

One possible explanation of the phenomenon is as follows. Suppose we assume that the amine picrates can exist in two forms, a molecular addition compound $R_3N \cdot HPI$ and a salt-like form, $R_3HN^+ \cdot Pi^-$. Then the solute is really a mixture of electrolyte and non-electrolyte, and the equivalent conductance calculated on the basis of total solute concentration would be apparently too low. We have the following equilibria



If we let $[R_3N] = [HPI] = c\alpha$ and $[R_3HN^+] = [Pi^-] = c\gamma$, and neglect long range interionic forces, the following equations must apply

$$c\gamma^2/(1 - \alpha - \gamma) = K \quad (4)$$

$$c\alpha^2/(1 - \alpha - \gamma) = k \quad (5)$$

where K is the dissociation constant characteristic of the electrolyte, and k that for the molecular compound.^{6a} The conductance equation then becomes (if we neglect the conductance of the picric acid, which certainly is a very weak electrolyte in tricresyl phosphate)

$$\frac{1}{\Lambda} = \frac{c\Lambda}{K\Lambda_0^2} + \left(1 + \sqrt{\frac{k}{K}}\right) \frac{1}{\Lambda_0} \quad (6)$$

That is, $1/\Lambda$ is a linear function of $c\Lambda$, with the usual slope, but the intercept is larger than $1/\Lambda_0$ by an amount depending on the ratio of the two dissociation constants. Examples are shown in Fig. 4; it will be seen that the curves resemble ordinary $1/\Lambda - c\Lambda$ plots, except in the magnitude of the ordinates. From the slopes and intercepts, we obtain the results given in Table III, assuming $\Lambda_0 = 2.00$ for all the compounds.

Lead abietate also has been included; we cannot assume a non-polar dissociation in this case but if we assume a non-polar modification of lead abietate to exist, the conductance equation becomes

$$\frac{1}{\Lambda} = \frac{c\Lambda}{K\Lambda_0^2(1 - \beta)} + \frac{1}{\Lambda_0(1 - \beta)} \quad (7)$$

if β is the fraction of solute present as undissociable compound.

TABLE III

CONSTANTS FOR ELECTROLYTES IN TRICRESYL PHOSPHATE

Salt	Λ_0	$K \times 10^6$	k
Bu ₄ NPI	1.95	1.014
Bu ₃ HNPI	1.73	0.118
Bz ₃ HNPI	(2) ^a	.439	0.00297
PhH ₃ NPI	(2)	.0444	.0529
Ph-C ₆ H ₄ -H ₃ NPI	(2)	.0295	.0118
PhMe ₂ HNPI	(2)	.0295	.0118
PbAb ₂	(2)	.0022	(.00059) ^b

^a By assumption. ^b $(1 - \beta)$ instead of k .

Based on the assumption underlying Eq. (6), we find that the electrolytic form of tribenzylammonium picrate is considerably stronger than the tributyl salt, while the aromatic picrates are much weaker. The assumption of some molecular compound in the tributyl salt would

(6a) It will be noted that a third equilibrium constant, that corresponding to $[R_3N \cdot HPI] \rightleftharpoons [R_3HN^+ \cdot Pi^-]$ has been suppressed here. The present data permit evaluation of only two empirical constants, and for simplicity, the third constant, which would appear as a factor in the denominator for Eqs. (4) and (5) has been dropped.

also account for the observed inversion of Λ_0 values for Bu_3HNPI and Bu_4NPI .

It has been known for some time⁷ that aniline picrate exists in two forms with different solubilities, but no account of electrical properties has been published.⁸ Pedersen suggested that the two forms might be molecular addition compound and electrolyte, but in view of the color change which occurs⁹ when "organic nitro compounds form addition products with aromatic molecules" was inclined to doubt the hypothesis. The present work, however, clearly shows that these picrates exhibit electrical anomalies, which easily can be accounted for by the assumption of two isomeric structures, which differ in the location of a proton. Further work, suggested by the present data, is planned.

Another group of electrolytes has been long known, which exhibit a similar behavior. The heavy metal cyanides in liquid ammonia¹⁰ have

(7) K. J. Pedersen, *THIS JOURNAL*, **56**, 2615 (1934).

(8) An abnormally low conductance of aniline picrate in nitrobenzene has been observed. The conductance was greatly increased by adding either amine or picric acid, which indicates the displacement of an equilibrium, and is excellent evidence in favor of the existence of a molecular compound. We are indebted to Dr. C. A. Kraus of Brown University for this information.

(9) Pfeiffer, "Organische Molekülverbindungen," 1922, pp. 218-245.

(10) Franklin and Kraus, *THIS JOURNAL*, **27**, 197 (1905).

low equivalent conductances, which are nearly independent of concentration over a wide range of dilution. It is obvious that the assumption of polar and non-polar isomers for these compounds could account for the experimental facts.

Summary

1. The conductances at 40° and 60 cycles in tricresyl phosphate of the following salts have been determined: tetrabutyl-, tributyl-, tribenzyl-ammonium, *p*-phenylaniline-, dimethylaniline and aniline picrates, and lead abietate.

2. Tetrabutyl- and tributylammonium picrates give practically normal conductance curves. Two anomalies appear, however: the product of limiting equivalent conductance and viscosity for the tetra salt in tricresyl phosphate is about 30% larger than for the same salt in ethylene chloride, and the conductance curve satisfies the equations derived on the basis of a simple binary ionic association over an unexpectedly wide range of concentration.

3. The picrates of the aromatic amines and lead abietate give conductance curves which suggest that they exist in two modifications, one of which cannot furnish ions.

SCHENECTADY, N. Y. RECEIVED NOVEMBER 23, 1938

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Electron Diffraction Investigation of the Molecular Structures of Cyanogen Chloride and Cyanogen Bromide

BY J. Y. BEACH¹ AND ANTHONY TURKEVICH²

The decrease of interatomic distances below the values expected from the table of covalent radii^{3,4} has been observed in several compounds.^{5,7} This shortening has been discussed in terms of multiple bond character and the resonance of molecules among several electronic structures.^{4,8} It seemed to us possible that this effect might also be observed in the case of the cyanogen halides, ClCN and BrCN . To investigate this we have

(1) National Research Council Fellow in Chemistry.

(2) Cramer Fellow from Dartmouth College.

(3) Pauling and Huggins, *Z. Krist.*, (A) **87**, 205 (1934).

(4) Pauling and Brockway, *THIS JOURNAL*, **59**, 1223 (1937).

(5) Brockway and Wall, *ibid.*, **56**, 2373 (1934).

(6) Brockway and Beach, *ibid.*, **60**, 1836 (1938).

(7) Gregg, Hampson, Jenkins, Jones and Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

(8) Pauling, Brockway and Beach, *THIS JOURNAL*, **57**, 2705 (1935).

determined the interatomic distances in these molecules by electron diffraction.

The apparatus used was that described by Beach and Stevenson.⁹ The electrons were accelerated by 41 kilovolts and their wave length, 0.0590 Å., was determined accurately from transmission pictures of gold foil ($a_0 = 4.070$ Å.). The diffraction patterns were recorded on photographic plates 12.19 cm. from the nozzle. The interpretation of the diffraction pattern was carried out by the visual method¹⁰ as well as by the radial distribution method¹¹ and a modification of the latter.¹²

(9) Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

(10) Pauling and Brockway, *ibid.*, **2**, 867 (1934).

(11) Pauling and Brockway, *THIS JOURNAL*, **57**, 2684 (1935).

(12) Degard, *Bull. soc. sci. Liège*, **2**, 115 (1938); Schomaker, *THIS JOURNAL*, to be published.