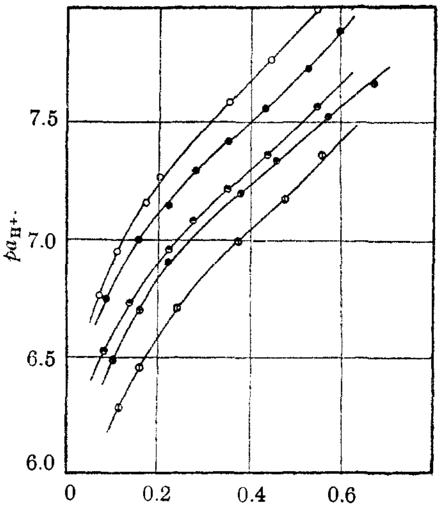

Fig. 1.—Brom thymol blue: ⦶, water; ⊕, 20% glycol; ⊖, 10% ethanol; ●, 40% glycol; ○, 20% ethanol.

discussed by Harned and Owen,[14] but no satisfactory general theory has yet been advanced to explain all of the observed facts. A regular, though non-linear, increase in the ionization constants of several aliphatic acids has been observed with change in $1/D$ when an organic solvent is mixed with water in increasing proportions.

Our work shows the specific effect of the organic solvent. Ten per cent. ethanol and 20% glycol have the same dielectric constant, but thymol blue shows pK values of 1.63 and 1.70 in the two solvents, while brom thymol blue has pK values of 7.49 and 7.42. Thus, 10% ethanol has less effect on thymol blue than 20% glycol, and more effect on brom thymol blue than 20% glycol. Exactly the same effect is seen by comparing values in 20% ethanol and 40% glycol, solvents of equal dielectric constant. Therefore, no general conclusions can be drawn until more data are accumulated with the same indicators in other hydroxy solvents and with other indicators.

The results may be briefly compared with some previous values. Kolthoff[6] has evaluated the various reported values of indicator constants in aqueous solutions and gives as best, values of 1.65 for thymol blue and 7.15 for brom thymol blue at an ionic strength of 0.05. The same author has calculated from experimental data the ethanol correction factor which must be applied in the colorimetric determination of pH. At 10–20° he gives an alcohol correction of 0.00 and +0.02 for thymol blue in 10 and 20% alcohol by volume. No work has been reported in glycol.

Summary

1. Electromotive force measurements have been made at 25° on the cell Pt | H_2 | Solution | AgCl | Ag in five solvents, water, 10% by weight ethanol, 20% by weight ethanol–water, 20% by weight ethylene glycol–water, and 40% by weight ethylene glycol–water.

2. Hydrogen ion activities have been calculated from the electromotive force measurements and used, along with spectrometric measurements, to determine the apparent indicator constants of thymol blue (acid range) and brom thymol blue in the above five solvents.

CHAPEL HILL, N. C.

RECEIVED JUNE 11, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Exchange Reactions between *p*-Nitrobenzyl Halides and Halide Ions[1]

BY TOM A. BITHER,[2] JULIAN M. STURTEVANT[3] AND HENRY C. THOMAS

The mechanisms of several simple types of organic reactions have been studied through the aliphatic halides. Displacement reactions of these compounds have been the subjects of numerous investigations, as, for example, in the work of Conant, Kirner and Hussey,[4] Young and Olson,[5] Koskoski, Dodson and Fowler,[6] Elliot and Sugden,[7] Seelig and Hull,[8] and many others.[9] The study of the kinetics of such reactions has produced significant information on reaction mechanism, for example, the well-known proof that the Walden inversion proceeds by a substitution mechanism.

With the hope of uncovering regularities in a limited but inclusive field, a study has been made of the kinetics in acetone–water solutions of the four possible displacement reactions between *p*-nitrobenzyl chloride and bromide and the chloride and bromide ions

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(1) This paper is based on the dissertation presented in 1942 to the Faculty of the Graduate School of Yale University by Tom A. Bither in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(4) Conant, Kirner, and Hussey, THIS JOURNAL, **47**, 488 (1925).

(5) Young and Olson, *ibid.*, **58**, 1157 (1936).

(6) Koskoski, Dodson and Fowler, *ibid.*, **63**, 2149 (1941).

(7) Elliot and Sugden, *J. Chem. Soc*,, 1836 (1939).

(8) Seelig and Hull, THIS JOURNAL, **64**, 940 (1942).

(9) A rather complete bibliography of work on the kinetics of displacement reactions is to be found in Tom A. Bither, Dissertation, Yale University, 1942.

$$\mathrm{RX} + \mathrm{Y}^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{RY} + \mathrm{X}^-$$

The velocity constants k_1 and k_2 are, of course, equal for isotopic exchange (X = Y). Reactions of these types have been repeatedly shown to follow a second order law.[7,8] If a and b are the initial molar concentrations of organic halide and halide ion, respectively, the rate equation for the case of isotopic exchange is

$$k = \frac{1}{(a+b)t} \ln \left\{ a \middle/ \left[a - (a+b)\left(\frac{x}{b}\right) \right] \right\}$$

in which x is the molar concentration of displaced halide. Here the term x/b is the experimental measure of the extent to which the reaction has proceeded at time t. In our experiments x/b was determined by a ratio of radioactivities measured with a Geiger–Müller counter.

For the hetero-exchange the integrated velocity equation may be put in the form

$$k = \frac{K_1}{t\sqrt{A}} \ln \frac{2(K_1 - 1)x - K_1(a+b) - \sqrt{A}}{2(K_1 - 1)x - K_1(a+b) + \sqrt{A}} \quad \frac{K_1(a+b) - \sqrt{A}}{K_1(a+b) + \sqrt{A}}$$

in which

$$A = K_1^2(a+b)^2 - 4abK_1(K_1 - 1)$$

and $K_1 = k_1/k_2$. Here the experimentally measured quantity is x, again the number of moles of chloride or bromide ion displaced from the organic halide at time t. This quantity was in most cases determined by means of an indirect analysis involving the weights of mixed silver halide precipitates obtained before and during the course of the reaction.

Experimental

Materials.—Since it has been shown[10] that traces of water in solvent acetone have a large effect on the velocity of reactions of the type with which we are here concerned, a solvent containing, by volume, nine parts of acetone and one part of water was chosen for this work. Reagent acetone was refluxed for several hours over potassium permanganate, distilled, and dried over anhydrous potassium carbonate. It was then redistilled through a Widmer column and the middle fraction collected for use. Since all solutions were made up at room temperature, volume corrections to take into account changes in concentration were applied where necessary. The volume coefficient of expansion of the acetone–water mixture was taken to be 0.0014 per degree, as determined by Le Roux and Sugden.[10] It was assumed that the dilute solutions used in the velocity measurements had the same coefficient.

The *p*-nitrobenzyl chloride used was Eastman Kodak Co. White Label product. It was recrystallized from 95% ethanol and dried *in vacuo* over calcium chloride. The purified material melted from 72–72.5°. The *p*-nitrobenzyl bromide, likewise Eastman White Label, was treated once with Norite in 95% ethanol and recrystallized twice from this solvent. After drying *in vacuo* over calcium chloride the product melted from 97.5–98.5°.

Lithium chloride and lithium bromide supplied the halide ions for the reactions. Lithium chloride containing radioactive chloride was prepared in the following manner. For each sample desired a target of potassium chloride, prepared by fusing 0.2–0.3 g. of the salt into a small gold foil cup, was subjected to deuteron bombardment for about forty-five minutes.[11] The radioactive sample was rapidly converted to hydrogen chloride which was absorbed in the calculated amount of lithium carbonate solution. (Merck lithium carbonate was recrystallized from water to reduce the foreign metal content.) Exact neutralization of the resulting solution, evaporation to dryness, and gentle ignition to destroy organic matter gave a radioactive lithium chloride which could be freed from charred matter by dissolution in water and filtration. On evaporation to dryness a salt containing chlorine as the only radioactive element was obtained. Direct bombardment of lithium chloride is disadvantageous on several counts: the lithium salt is partially volatilized during bombardment; radioactive impurities are acquired from the cyclotron; any trace of sodium in the lithium preparation becomes strongly activated and may vitiate the measurements entirely.

Since deuterons of sufficient energy to activate bromine nuclei directly were unavailable to us, the radioactive lithium bromide used in this work was prepared via the Szilard–Chalmers[12] technique. Approximately five liters of ethylene dibromide, surrounded by paraffin, was irradiated during three to four and a half hours by neutrons from a beryllium–deuteron source. Immediately following irradiation the ethylene dibromide was extracted with 100 ml. of a water solution containing about 1 g. of lithium bromide. (This lithium bromide was prepared from recrystallized lithium carbonate by treatment with "Analyzed" grade hydrobromic acid.) A second extract in 100 ml. of water only was combined with the first. The solution was carried to dryness, charred, redissolved, filtered, and carried to dryness a second time to obtain a sample of lithium bromide of high specific activity.

The Radioactivity Measurements.—The majority of the radioactivity measurements were made with a Geiger–Müller counter actuating a Neher–Harper circuit[13] followed by a thyratron scale-of-two and a Kerst scale-of-ten.[14] Scale factors of two, ten, or twenty could be obtained with this apparatus. In a few of the later measurements a "hard tube" scale-of-thirty-two circuit employing self-quenching counters was used. The counter tube (copper cylinders in argon–xylene or argon–alcohol) were of all glass construction and consisted of the counter proper surrounded by a jacket to contain radioactive solutions. This construction ensures reproducible geometry. Care was taken that all solutions measured were of chemical composition closely similar to their corresponding standards; no uncertain corrections for absorptive losses were necessary. Both benzene and acetone–water solutions were used in the activity measurements. Preliminary measurements on benzene, acetone, and water solutions containing equal concentrations of radioactive material showed that in dilute solutions the counting rate was the same, within normal fluctuations, for all three solvents. It was therefore unnecessary to apply correction factors in going from one solvent to another.

As a check on the apparatus the half-lives of Cl^{38} and Br^{82} were determined several times during the course of the work. A typical determination on chlorine gave 37.6 minutes which compares well with the recent value of 37.5 minutes given by Curran, Dee and Strothers.[15] The counting was carried out over a period of four to five half-lives; counting rates varied from 3600/min. to 230/min. For the half-life of the long-lived bromine isotope a value of 36.2 hours was found. This value agrees with the value of 36 hours reported by Roberts, Downing and Deutsch.[16]

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[10] Le Roux and Sugden, *J. Chem. Soc.*, 1279 (1939).

[11] For the radioactivity preparations used in this work we are indebted to the cyclotron staff of the Sloane Physics Laboratory of Yale University. These preparations were made possible by grants from the George Sheffield Fund of Yale University.

[12] Szilard and Chalmers, *Nature*, **134**, 462 (1934).

[13] Neher and Harper, *Phys. Rev.*, **49**, 940 (1936).

[14] Kerst, *Rev. Sci. Inst.*, **9**, 132 (1938).

[15] Curran, Dee and Strothers, *Proc. Roy. Soc.* (London), **174**, 546 (1940).

[16] Roberts, Downing and Deutsch, *Phys. Rev.*, **60**, 544 (1941).

The numerical treatment of the counting data was carried out by use of the convenient "counting function"

$$F \equiv \frac{\Delta N/1000}{1 - \exp(-\lambda\delta)}$$

in which ΔN is the observed number of counts (corrected for the background of the counter); λ, the disintegration constant of the isotope in question; and δ, the time interval of the count of ΔN. This function, immediately derivable without approximation from the first order disintegration law, changes with the time, say, of the start of the counting interval in the same way as does the actual number of radioactive nuclei present and thus may be easily calculated to a standard time for the comparison of results. If one makes use of a large table of exponentials, this function is perhaps the most convenient form in which to express counting results. It also may serve as a means for the determination of the decay constant. All that is needed is a rough preliminary value of λ to be used to initiate a short series of successive approximations.

The Rate Measurements.—The reactions were carried out in λ-shaped tubes each arm of which had a capacity of about 40 ml. Solutions of the nitrobenzyl halide and of the lithium halide in the acetone–water solvent were introduced into the two arms of the tube and, after a sufficient time in the thermostat to attain temperature equilibrium, were mixed by shaking. At the end of the reaction interval the contents of the tube were rapidly and quantitatively transferred to a separatory funnel containing 125 ml. of water and 35 ml. of benzene and were vigorously shaken. The benzene layer containing the nitrobenzyl halide was carefully washed with two 30-ml. portions of water and diluted to a volume of 50 ml. for the radioactivity measurements. The water layer was titrated for halide with silver nitrate. Preliminary extractions of known mixtures of lithium halide and organic halide followed by determinations of halide ion and of organic halide in the extracts showed that with the exercise of reasonable care recoveries of sufficient completeness were obtainable.

The reactions were carried out in a water thermostat maintained at the desired temperature to ±0.05° by means of a large mercury-in-glass regulator with a vacuum tube relay.

All reactions were timed with an electric clock possessing a large dial swept by a second hand. The same clock was used in the counting measurements.

The course of the reactions between *p*-nitrobenzyl chloride and the bromide ion and between *p*-nitrobenzyl bromide and the chloride ion was followed by chemical analysis. Weights of mixed silver halides were determined, and the extent of the reaction was calculated from the excess or defect in weight as compared to the weight of silver halide from a sample of the initial lithium halide solution.

Errors.—The principal error in the determination of the velocity constants in most cases is the uncertainty in the timing of the reaction. The accuracy of the timing was determined by the time required to start and quench the reaction. The starting time was uncertain by no more than five seconds, the time required to mix the contents of the reaction vessel. For reactions in which glass stoppered tubes were employed the quenching time was also in the neighborhood of five seconds. However, for reactions carried out at temperatures of 50 and 70° sealed tubes were necessary, and the reaction was "stopped" by cooling the tube in an ice-salt bath. Since the rate constants at 50° are some 100 times larger than those at 0°, this method was assumed to stop the reaction effectively. The timing error in these cases is necessarily large and is difficult to estimate. For reactions carried out in glass stoppered tubes for periods of more than nine minutes the timing error is probably less than 1%.

Errors in the determination of the extent of the reaction are of significance. In the radioactivity measurements whenever possible more than 10,000 counts were taken to reduce the uncertainty due to fluctuations to about 1%. In the chloride-chloride exchanges the reactions are quite slow. Because of this and because of the short half-life of radiochlorine it was not always possible to obtain 10,000 counts. Thus the uncertainty in a determination of the extent of reaction for an isotopic exchange is of the order of 2–3% and may be greater. In the cross exchange reactions ($RCl-Br^-$, $RBr-Cl^-$) the analysis was carried out by the notoriously uncertain indirect method. The change in weight of the silver halide during the course of a reaction was usually less than two milligrams. During the initial stages of the reaction the error due to the small weight differences was so large that the velocity constants calculated from such differences were arbitrarily omitted in calculating the average values of the specific reaction rates.

Other chemical errors involved in the preparation and analysis of the solutions were small. Nitrobenzyl halide solutions were prepared by weighing the compounds into calibrated volumetric flasks. Lithium halide solutions were titrated for halide content. Chloride was determined by direct titration with silver nitrate using potassium chromate as indicator; bromide was determined by the Volhard method.

Since it is difficult if not impossible to estimate the effect on a determination of a velocity constant of all the possible individual errors and since we have discovered no large systematic errors in the results, the scattering of the individual determinations as measured by the standard deviation is perhaps the best indication of the accuracy of the results. In most cases an accuracy of 10% or better is thus indicated.

Results

For purposes of illustration the complete data on four representative experiments are given in Tables I and II. Table I presents the data and results of two experiments on isotopic exchange. Due to the slowness of the chloride exchange and the short half-life of radiochlorine, it was impossible to follow the chloride exchanges beyond the initial period of the reaction. Our experiments cannot be said to demonstrate the second order of this reaction, since we have not largely varied the concentrations of the reactants; however, we have assumed the second order character since it has been demonstrated for similar reactions.[7,8] The ratio of the concentrations of the reactants in the more rapid bromide exchange was varied seven fold. The standard deviations of the velocity constants determined at 0, 15, 25, and 30° are 4.4, 5.2, 10.3, 4.2%, respectively. The results do not, therefore, deviate from a second

TABLE I

ISOTOPIC EXCHANGES

$RCl-Cl^-$

Temp. 30.00 ± 0.03°; [RX] = 0.05771 mole/liter; [LiX] = 0.01146 mole/liter.

Sample	Total counts	δ (min.)	$F(t_0)$	Reaction time, min.	% completion	$k \times 10^4$ (liters/mole. sec.)
1	4220	90	156	120	1.0	0.198
2	1250	90	263	214	1.6	.187
Standard	11511	50	19106			
$RBr-Br^-$						
Temp. 30.00 ± 0.05°; [RX] = 0.01064 mole/liter; [LiX] = 0.02903 mole/liter.						
1	13638	60	6779	5	35.0	362
2	15181	42	11015	10	56.9	353
3	15593	31	13942	15	72.1	357
4	17047	57	16354	20	84.5	392
Standard	45871	30	72134			

order law beyond a reasonable estimate of the accuracy of the experiments. In Table II are given typical results of experiments on mixed exchanges in which analysis was carried out by the indirect procedure. In these cases, again, we have no results which indicate other than a second order reaction.

TABLE II

MIXED EXCHANGES

RCl–Br^-

Temp. 30.00 ± 0.05°. Initially [RCl] = 0.06120 mole/liter; [LiBr] = 0.04003 mole/liter. Volume of reaction sample, 47.07 ml.

Sample	AgCl + AgBr, g.	Reaction time, min.	$[Cl^-]$ (mole/liter)	$k \times 10^4$ (liters/mole. sec.)
Standard	0.3542			
2	.3500	60	0.00200	(2.38)
3	.3484	120	.00276	(1.70)
4	.3468	180	.00355	1.50
5	.3450	240	.00440	1.45
6	.3430	300	.00535	1.50
7	.3410	390	.00631	1.46
8	.3390	540	.00727	1.34

RBr–Cl^-

Temp. 30.00 ± 0.05°. Initially RBr = 0.05289 mole/liter; [LiCl] = 0.04169 mole/liter. Volume of reaction sample, 46.60 ml.

Sample	AgCl + AgBr, g.	Reaction time, min.	$[Cl^-]$ (mole/liter)	$k \times 10^4$ (liters/mole. sec.)
Standard	0.2785			
1	.2850	12	0.00313	21.2
2	.2904	24	.00575	20.7
3	.2949	36	.00792	20.0
4	.3012	48	.01097	22.7
5	.3044	60	.01251	21.7
6	.3086	72	.01453	22.3
7	.3101	84	.01526	20.5
8	.3130	96	.01665	20.5
9	.3151	108	.01766	20.0

Table III summarizes the results of all experiments in the form of average specific reaction rates and standard deviations.

TABLE III

SPECIFIC REACTION RATES

Temp., °C.	No. of measurements of k	$k \times 10^4$ (liters/mole. sec.)
	RCl–Cl^-	
30.00±0.05	5	0.181 ± 0.011
50.00±0.05	4	1.423 ± 0.048
70.00±0.05	6	10.14 ± 0.61
	RCl–Br^-	
30.00±0.05	24	1.35 ± 0.13
50.00±0.05	10	6.72 ± 0.93
	RBr–Cl^-	
0.04±0.02	6	0.810 ± 0.037
30.00±0.05	16	21.4 ± 1.7
50.00±0.05	20	132 ± 11
	RBr–Br^-	
0.04±0.02	11	12.86 ± 0.56
15.00±0.05	8	64.3 ± 3.3
25.00±0.04	5	174 ± 18
30.00±0.05	12	356 ± 15

Discussion

The data of the foregoing tables have been summarized by the application of the simple collision theory formula for the velocity constant of bimolecular reactions

$$k = D^2 \left[\frac{8\pi RT}{M}\right]^{1/2} e^{-E_m/RT}$$

in which M is the reduced molecular weight of the two reacting species; D, a "molecular diameter"; and E_m, the appropriate minimum energy necessary for reaction. The constants of the empirical Arrhenius equation

$$k = Ae^{-E_a/RT}$$

have also been computed. In this equation E_a is the activation energy. These calculations were carried out by the method of least squares (in three cases), weighting the data according to the number of determinations of k. Table IV gives these results.

TABLE IV

PARAMETERS OF SPECIFIC RATE EQUATIONS

	Collision equation		Arrhenius equation	
	D, Å.	E_m, cal.	A, liters/mole. sec.	E_a, cal.
RCl–Cl^-	1.10	20,500	1.79×10^{10}	20,820 ± 700
RCl–Br^-	0.05	15,330	2.52×10^{7}	15,640 ± 2000
RBr–Cl^-	1.07	17,570	1.61×10^{10}	17,870 ± 500
RBr–Br^-	5.71	17,750	3.30×10^{11}	18,030 ± 800

There is little to choose between the two equations as to the manner in which they reproduce the data. For the RBr–Br^- reaction the collision formula gives the following percentage deviations from the observed constants: 0.04°, −5%; 15°, +6%; 25°, +13%; 30°, −8%. The Arrhenius formula gives the deviations: −4, +8, +14, −8%. The standard deviations calculated directly from the experimental results are, in these four cases, 4, 5, 10, 4%. The results in the other cases in which the comparison is of significance are similar.

It is to be noted that little regularity appears in the energy parameters of these formulas. Furthermore the low pre-exponential factor for the RCl–Br^- exchange gives the excessively low collision diameter of 0.05 Å. in this case. In other terms, however, the results appear to be not inconsistent. Using the Arrhenius equations and putting $\Delta H^{\ddagger} = E_a - RT$ the thermodynamic functions for the activated complexes have been calculated according to the methods of Eyring and his coworkers.[17] Table V gives the results of these calculations.

The free energies of activation change in a regular fashion and are consistent with the known smaller reactivity of the chloride compounds. The large entropy change for the RCl–Br^- reaction (reflected in the low collision diameter) appears surprising. Unfortunately this result is associated

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[17] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

TABLE V

THERMODYNAMIC FUNCTIONS FOR THE ACTIVATED COMPLEXES AT 298.16°K.

	$\Delta H^{\ddagger}$, cal./mole	$\Delta F^{\ddagger}$, cal./mole	$\Delta S^{\ddagger}$, cal./mole. deg.
RCl–Cl⁻	20,220	24,280	−13.6
RCl–Br⁻	15,040	23,000	−26.7
RBr–Cl⁻	17,280	21,400	−13.8
RBr–Br⁻	17,440	19,780	− 7.8

with the least precise of the sets of velocity determinations. Unpublished results obtained independently in this Laboratory appear to confirm this specific effect. A similar large difference has been found between the entropies for the nitrobenzyl chloride–bromide ion and the nitrobenzyl bromide–chloride ion reactions in a 95–5 (by volume) acetone–methanol solvent containing about 0.6% water. More work is necessary on this point before a complete discussion can be given. An analogous system of reactions investigated in a very precise fashion by Young and Olson[6] shows no such large entropy differences. It should, however, be pointed out in this connection that the halogen of the substituted acetic acids investigated by these workers has a very different reactivity from that of the benzyl halides of the present work. Comparisons between such different compounds are on a very insecure basis.

Summary

1. The rates of the exchange reactions between *p*-nitrobenzyl chloride and *p*-nitrobenzyl bromide and the chloride and bromide ions have been measured in acetone water solutions over various temperature ranges.

2. The results have been analyzed from the point of view of the theory of the activated complex.

NEW HAVEN, CONNECTICUT RECEIVED MARCH 22, 1945

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

Electrical Properties of Solids. XV. Electrolytes in Plastics[1]

BY DARWIN J. MEAD AND RAYMOND M. FUOSS[1a]

I. Introduction

In-phase components of current give rise to a.c. power losses in dielectrics; they can be produced either by ionic conductance or by relaxation phenomena of one sort or another. Measurements by a.c. methods give total losses, while d.c. measurements can only give currents produced by actual transport of charged particles. As a first approximation, the relaxation effects can be determined by subtracting the d.c. current from the total a.c. in-phase current; however, as we pointed out early in this series,[2] the difference may still contain contributions due to the electrolyte present. Best proof of this statement is found in the fact that both dielectric constant and a.c. loss factor vary in a systematic way with d.c. conductance, when appreciable quantities of electrolyte are present.

In our early work, the electrolyte was frequently hydrogen chloride of unknown concentration produced by pyrolysis of polyvinyl chloride during the preparation of the samples. In other cases, the nature of the electrolyte was also unknown; it could have been traces of catalysts or emulsifiers, for example. We therefore started a systematic study of the problem, using known concentrations of known electrolytes in plastics as the solvent medium.

It is the purpose of this paper to present some exploratory work on the system polyvinylchloride–diphenylmethane (80:20)–tetrabutylammonium picrate (10^{-4} to 0.05 *N*), which was done before pressure of war work caused us to postpone further studies. We are not yet able to describe the results in terms of a molecular model, but we have at least succeeded in defining conditions under which reproducible a.c. and d.c. results can be obtained on high-loss dielectrics, a problem of considerable technical importance.

II. Experimental

The **polyvinyl chloride** was similar to sample A5 which has been described previously.[3] Diphenylmethane[4] was chosen as plasticizer, because it is relatively high-boiling and non-polar. **Tetrabutylammonium picrate**[5] was selected as a typical strong electrolyte which is soluble in non-aqueous systems.

Samples for the electrical measurements were disks 5 cm. in diameter and usually 2–3 mm. thick. Polymer and plasticizer were weighed out separately in proportions 80:20, and salt (or a 1% or 0.1% solution of salt in Ph_2CH_2) was weighed into the plasticizer. The amounts of salt were taken to give round values of concentration, calculated on a normality basis using 1.316 as the density[4] of the 80:20 plastic. No correction was made for the volume of salt because the highest concentration was only 0.05 *N* (23.52 g./l.). Several volumes of methanol were added (petroleum ether, used in our previous work,[4] precipitates the picrate) to dilute the salt solution, which was then added to the polymer, and a little more methanol was used to complete the quantitative transfer. The mixture was stirred five minutes to distribute salt and plasticizer uniformly, and then the methanol was evaporated by

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[1] Paper XIV, THIS JOURNAL, **65**, 2067 (1943).

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[2] Fuoss, THIS JOURNAL, **61**, 2329 (1939).

[3] Fuoss, *ibid.*, **63**, 2401 (1941).

[4] Mead, Tichenor and Fuoss, *ibid.*, **64**, 283 (1942).

[5] Mead and Fuoss, *ibid.*, **61**, 2047 (1939).