[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Electrolytic Conductance by Proton Jumps: The Transference Number of Barium Bisulfate in the Solvent Sulfuric Acid[1]

BY LOUIS P. HAMMETT AND FREDERICK A. LOWENHEIM

With the exception of migration phenomena, our knowledge of the properties of absolute sulfuric acid as an ionizing solvent is reasonably complete and consistent.[2] The solvent is so acidic that water and most organic oxygen compounds are completely converted to ionized oxonium bisulfates by reactions of the type

$$H_2O + H_2SO_4 \rightleftharpoons OH_3^+ + HSO_4^-$$

and that salts containing any other anion are converted to bisulfates by such reactions as

$$NaCl + H_2SO_4 \rightleftharpoons Na^+ + HSO_4^- + HCl$$

The somewhat surprising situation that concentrated (0.1 to 1 molal) solutions exhibit simple regularities of behavior which disappear in more dilute ones has been shown[2] to result from the extraordinarily small magnitude of interionic forces in this medium combined with the large self-ionization of the solvent. In the more concentrated solutions the solvent ionization, which likewise produces bisulfate ion, is so completely suppressed by the added bisulfate ion that it is no longer a factor; and it is then found that ions behave with respect to freezing point, solubility, and conductivity[3] as practically ideal solutes. The statement of Hantzsch,[4] the pioneer in the investigation of these solutions, that no migration can be demonstrated presented, however, a discrepancy which we have now removed by showing that the barium ion in a solution of the typical solute barium bisulfate does indeed migrate toward the cathode. The extraordinarily low value of the cation transference number found, about 0.007, not only explains Hantzsch's conclusion, but is of considerable interest in connection with the problem of the excess mobility of hydrogen and hydroxyl ions in water.

Method and Materials

Apparatus.—The Hittorf method was of necessity employed because the more precise and elegant moving boundary method of MacInnes[5] and co-workers presupposes an already fairly accurate knowledge of at least two relative ion mobilities, information completely lacking for this solvent. A further disadvantage inherent in the solvent is the lack of electrodes at which gas evolution does not occur, electrodes of properties comparable to those of the silver–silver chloride electrode in water (cadmium amalgam, mercury and silver all reduce sulfuric acid). The platinum electrodes we have used provide steady currents, and the apparatus was designed to minimize the mixing effect of the inevitable gas evolution. The gas evolution is accompanied by the formation of sulfur and of sulfur dioxide at the cathode and of ozone and other oxidizing agents at the anode.

Some light is thrown on the notorious difficulty of obtaining consistent results by the Hittorf method, and on the not obviously necessary complication of the apparatus which has been used by other workers, by the unexpected mixing effects which we observed in an apparatus consisting of a large U-tube of 1.25 cm. bore provided with stopcocks of the same bore. When the yellow solution obtained by dissolving a very small amount of benzalacetophenone in absolute sulfuric acid is placed in the lower part of the tube and is brought into contact with superimposed colorless acid by opening the stopcocks, a column of yellow solution starts immediately to rise through the center of the colorless liquid. It mushrooms over at the top and in about an hour the whole tube shows an even yellow color. The same effect is observed when the positions of colorless and colored solutions are reversed, and it occurs also with aqueous solutions as may be shown by using dilute aqueous ammonia with one layer colored by phenolphthalein. Only when the lower layer is appreciably denser than the upper one does the effect disappear.

Our apparatus, shown in Fig. 1, consisted of anode, cathode, and middle chambers connected by narrower tubes whose sinuousity was found by experiments with colored solutions to prevent mixing of this sort. The vents for escape of the gases produced were protected from the atmosphere by tubes of glass beads wet with sulfuric acid which exerted no back pressure.

In the experiments in which trichloroacetic acid was used, these bead towers were replaced by absorbers to trap the decomposition products of the solute. At the cathode a small tube filled with pellets of potassium or sodium hydroxide was found satisfactory; at the anode, an inclined chain of ten bulbs, each partially filled with a strong solution of the alkali, was employed.

The current was between 10 and 25 milliamperes, and the quantity of electricity was measured by a copper coulometer.[6] The cells were immersed in a thermostat at 25°. At the end of a run the three portions were separated by

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[1] This article is based upon a dissertation submitted by Frederick A. Lowenheim to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1934. The material was presented at the Cleveland meeting of the American Chemical Society, September, 1934.

[2] Hammett and Deyrup, THIS JOURNAL, **55**, 1900 (1933).

[3] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907).

[4] Hantzsch, *Ber.*, **63**, 1789 (1930), esp. p. 1794.

[5] MacInnes and Longsworth, *Chem. Reviews*, **11**, 171 (1932).

[6] Creighton and Fink, "Electrochemistry," John Wiley and Sons, Inc., New York, 1928, Vol. I, p. 22.

air pressure through F and F′ and were sampled after being mixed thoroughly. The volumes of the anode and cathode portions could be read from the etched calibrations e, a, a′, etc.

As a check on possible diffusion, a run was made as follows: two cells (Figure 1) were set up with barium bisulfate solution in B and ammonium bisulfate solution of equivalent concentration in A and C. One cell was used as a blank, with no current, and through the other a current of 19 milliamperes was passed for thirty-five days. The end-portions were then analyzed for barium. The results are expressed in milligrams of barium sulfate per 10 g. of solution.

Blank 1	Blank 2	Run, Anode	Run, Cathode
1.4	7.2	2.7	66.5

Throughout the experiment, the two cells were kept side by side in the thermostat at 25°.

To demonstrate the applicability of the apparatus and method, the transference number of hydrogen ion in hydrochloric acid was determined by a rough experiment, using the same electrodes, coulometer, etc. The value obtained for an approximately 0.1 *M* solution was 0.878, which is a sufficiently close check, considering the absence of the usual refinements, on the accepted value of 0.828.

Methods of Analysis.—Barium was determined by weighing out portions of solution from a Bailey pipet, diluting with water and filtering through asbestos Gooch crucibles, which were ignited in a muffle furnace at 500–600°. Strontium was determined in the same way.

Trichloroacetic acid was determined essentially by the chromic–sulfuric acid distillation method of Robertson,[7] portions of the solution being weighed out by Bailey pipets. The apparatus of Robertson was altered along lines suggested by Mr. H. F. Fletcher. Bubble type absorbers were used, and all joints were of ground glass lubricated with sulfuric acid. After the chromic acid distillation and absorption in alkaline peroxide, the chloride was determined gravimetrically by means of silver nitrate.

Materials.—Absolute sulfuric acid was prepared by mixing 95% fuming acid with 30% fuming acid in approximately the proper proportions and adjusting by addition of water or fuming acid until the freezing point was above 10.35°. The product was protected against absorption of moisture from the atmosphere and tested by the freezing point.

Barium sulfate was prepared by the slow addition of barium hydroxide solution to dilute sulfuric acid, maintaining the solution always on the acid side. The precipitate was centrifuged, washed and ignited in a muffle at 450–500° in platinum dishes.

The solutions of barium bisulfate in sulfuric acid were made up to approximately the composition desired and analyzed. They were protected from atmospheric moisture except for momentary exposure during transfer to the cell. Their density was found to range from 1.886 to 1.907. The rounded off figure 1.9 was used in calculations since other factors limit the precision of the transference number to 5 or 10%.

Trichloroacetic acid was dried over phosphorus pentoxide for a week or more. Portions of a solution of it were analyzed by acidimetric titration and by a Mohr titration for chlorine following an alkaline hydrolysis. The ratios of moles of chloride ion to moles of acid found were 2.998 and 3.001, indicating freedom from significant amounts of other acids or chlorine compounds. An analysis of a dried sample of the acid by the chromic acid distillation method described gave a result 1.2% lower than the theoretical. The error probably results from the difficulty of weighing the hygroscopic material.

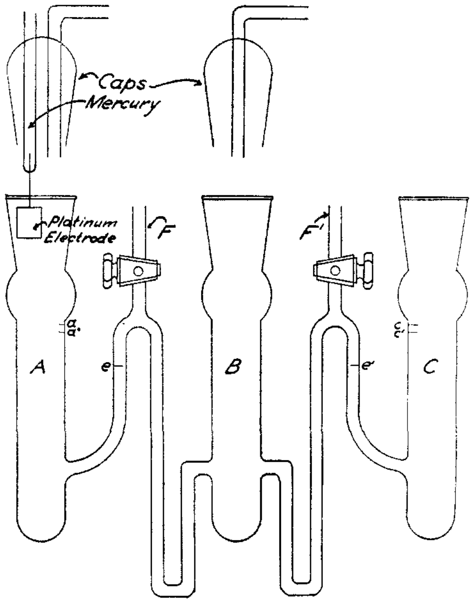

Fig. 1.

Potassium dichromate was recrystallized from water and dried at 120–130°. The hydrogen peroxide and potassium and sodium hydroxides used gave no test for chlorides.

Results

The Apparent Transference Number.[8]—Table I contains the detailed data and results on six determinations of the apparent transference number of barium in solutions of barium bisulfate of various concentrations. The analyses are given in grams of barium sulfate per gram of solution, *C* is the concentration of barium bisulfate in moles per liter, V_c and V_a are the volumes in cubic centimeters of catholyte and anolyte, from which the weights were calculated by using the density figure 1.9, Q is the quantity of electricity in coulombs, T_c, T_a and T are cathode, anode and average transference numbers, respectively. In Fig. 2 the transference numbers obtained in these six and in eight other experi-

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[7] Robertson, *J. Chem. Soc.*, **107**, 902 (1915); *Chem. News*, **120**, 54 (1920).

[8] We have called these quantities apparent rather than Hittorf transference numbers because it has been impossible to make the correction for effects accompanying the electrode reactions which is necessary for the calculation of a correct Hittorf number.

Table I

Apparent Transference Number of Barium Bisulfate

Expt.	C	Analyses Original	 Middle	 Anode	 Cathode
10	0.204	0.02503	0.02505	0.02410	0.02621
		2502	2513	2411	
		.02503	.02509	.02411	.02621
11	.204	.02509	.02501	.02422	.02599
		2497	2501	2422	2592
		.02503	.02501	.02422	.02596
12	1.01	.1229	.1229	.1226	.1239
		1229	1229	1225	1238
		.1229	.1229	.1226	.1239
13	1.01	.1229	.1229	.1229	.1241
		1228	1229	1230	1240
		.1229	.1229	.1230	.1240
14	0.092	.01134	.01126	.01042	.01234
		1134	1129	1044	1238
		.01134	.01128	.01043	.01236
15	.092	.01123	.01129	.009955	.01279
		1123	1129	9977	1279
		.01123	.01129	.009966	.01279

Expt.	V_c	V_a	Q	T_c	T_a	T
10	39	41	4956	0.0139	0.0127	0.0133
11	41	43.6	3823	.0160	.0142	.0151
12	39.4	41.5	4934	.0128	.0047	.00876
13	40.2	41.9	4132	.0179	0	.0090
14	41.8	44.2	4369	.0162	.0135	.0149
15	42.7	42.7	6676	.0151	.0133	.0142

ments are plotted against molar concentration of barium bisulfate. There is a strong indication of a definite variation of transference number with concentration, with a maximum in the neighborhood of 0.1–0.2 molar.

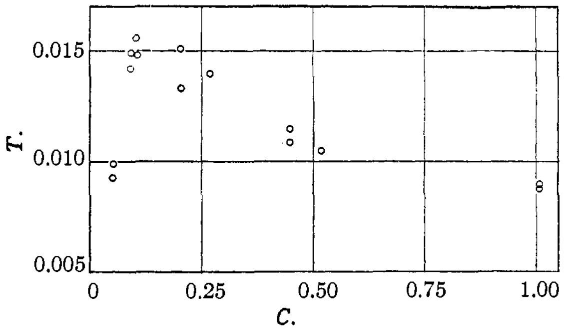

Fig. 2.—Apparent transference number and concentration.

Strontium Sulfate.—Table II contains the result of one determination of the transference number of strontium bisulfate in sulfuric acid. As was to be expected, the result is not materially different from that obtained with barium bisulfate.

Table II

Apparent Transference Number of Strontium Bisulfate

C	Analyses Original	 Middle	 Anode	 Cathode
0.31	0.03035	0.03063	0.02902	0.03205
	3070	3063	2913	3202
	.03053	.03063	.02908	.03204

V	V_a	Q	T_c	T_a	T
45.4	43.7	16,690	0.00766	0.00810	0.00788

The True Transference Number.—It is well known that the apparent transference number thus obtained may be an incorrect measure of the relative mobilities of the cation and anion through the medium, both because of volume changes which may accompany the electrode process and because of possible transfer of solvent with the moving ions. Since the differences between apparent and true transference numbers are absolute rather than relative, an apparent transference number as low as the one we have obtained might even differ in sign from the true transference number. That is, it is conceivable that the barium does not migrate, or even that it migrates toward the anode, and that the concentration changes observed are due entirely to transfer of the solvent toward the anode, or to changes in concentration produced by the electrode reactions. Both of these effects would be more pronounced in a solvent with the high molecular weight of sulfuric acid than they are in water.[9] That the electrode phenomena are significant is indicated by the consistently larger values obtained for transference into the cathode compartment than for transference out of the anode compartment. The determination of true transference requires the addition to the solution of a non-electrolyte and the determination of the concentration changes of the electrolyte with respect to this reference solute rather than with respect to the solvent. As a non-electrolyte we have used trichloroacetic acid, which has been shown both by conductivity and by cryoscopic methods to be a non-electrolyte.[2,3] Unfortunately the determination of this substance cannot be carried out with quite the high degree of precision which we obtained in the determination of barium, and we have been unable to find any other substance, non-ionized in this medium, which is susceptible to determination with higher, or indeed with comparable, precision. The results, which are given in Table III, do at least demonstrate the existence of a true

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[9] Washburn, This Journal, **31**, 322 (1909); see p. 352.

TABLE III

TRUE TRANSFERENCE NUMBER OF BARIUM BISULFATE

	Barium sulfate					Trichloroacetic acid								
		Analyses					Analyses							
Expt.	C	Original	Middle	Cathode	Δ_B, %	C	Original	Middle	Cathode	Δ_T, %	Q	V_c	T_{ap}	T_t
16	0.25	0.03102	0.03101	0.03363		0.28	0.02515	0.02441	0.02508					
		3108	3107	3345	8.05		2520	2426	2459	2.05	16,070	39	0.00953	0.0071
		.03105	.03104	.03354			.02518	.02434	.02484					
17	.25	Same	.03125	.03350		.28	Same	.02495	.02581					
		as	3115	3352	7.40		as	2470	2545	3.28	12,040	39	.0120	.0067
		16	.03120	.03351			16	.02483	.02563					
21	.42	.05085	.05091	.05323		.43	.03741	.03793	.03867					
		5091	5091	5324	4.58		3761	3730	3855	2.63	16,540	44.1	.00977	.0048
		.05088	.05091	.05324			.03751	.03762	.03861					
22	.42	Same	.05099	.05383		.43	Same	.03741	.03764					
		as	.05083	5390	5.81		as	3713	3749	0.81	19,170	44	.0107	.0092
		21	.05091	.05387			21	.03727	.03757					

migration of barium ion, and set a very low upper limit to its transference number.

In this table the column headings and units are the same as in Table I with the following additions: Δ_B and Δ_T are the percentage changes in concentration of barium bisulfate and of trichloroacetic acid, respectively; T_{ap} is the apparent transference number and T_t the true transference number of barium. The transference numbers are calculated from the transference into the cathode compartment only, because it was found that the trichloroacetic acid was so completely burned up at the anode that 90% or more of the total chlorine appeared in the absorbers. The chlorine content of the cathode absorbers was in every case less than 1% of the total cathodic chlorine, and the values given in the table for analyses of the catholyte are corrected for the chlorine found in the absorbers.

Precision.—The demonstration that transference exists and the precision of its determination depend upon the reliability with which small differences in concentration can be determined. The average deviation from the mean of all our barium determinations is about 1.2 parts per thousand; the difference in concentration between catholyte and anolyte (which is proportional to the transference numbers) varied from 2 to 16% of the concentration, and there is no reason to expect that any constant error should affect the analysis of cathode and anode portions differently. Compared with the probable error the differences are therefore quite sufficient to demonstrate transference, and the precision of the transference number obtained varies from 3 to 10%.

Similarly, the analyses of trichloroacetic acid have an average precision of 4 or 5 parts per thousand, which is sufficient to demonstrate that changes in concentration of trichloroacetic acid are not as great as of barium bisulfate.

In a medium as hygroscopic as sulfuric acid, the effect of possible contamination by water should not be neglected. The consistency of the results for the transference number would tend to indicate freedom from accidental contamination; but even if small amounts of water were present there is every reason to suppose that they would not interfere, for water has the same conductivity in sulfuric acid as other inorganic bisulfates, showing that oxonium ion must have approximately the same small mobility as barium ion, and that small amounts of oxonium ion would not sensibly lower the transference number of barium.

Discussion

It is quite impossible to account for the extraordinarily low transference number of barium ion by supposing that part of the barium is present in the form of a negatively charged complex ion, as is the case with cadmium iodide in aqueous solutions. Such a hypothesis is completely contradicted by the cryoscopic evidence that one molecule of barium bisulfate produces three ions in sulfuric acid solution.[2] The autocomplex formation would give not more than one ion per molecule, for instance

$$2Ba(HSO_4)_2 \rightleftarrows Ba^{++} + Ba(HSO_4)_4^-$$

This conclusion is further confirmed by the striking and hitherto unexplained fact that all of the scores of bisulfates, organic and inorganic, which have been studied in this medium, have practically identical conductivities.[10] Obviously even large variations in cation mobility can produce only small changes in total conductivity when the cation carries less than 1% of the current.

It is equally impossible to attribute the small transference of the barium ion to a high mobility of bisulfate ion in the sense of an actual motion of the latter, for the migration of one mole of bisulfate ion per faraday from the cathode compartment would result in the loss by that compartment of approximately one mole of sulfuric acid.[11] This loss in solvent is equivalent to an increase in concentration of the solute, the percentage change being 100 QM/FW where Q is the quantity of electricity traversing the cell, F is the faraday, M is the molecular weight of sulfuric acid, and W is the weight in grams of the catholyte. In the four experiments in which trichloroacetic acid was used, this formula predicts an increase in concentration in the cathode compartment varying from 16 to 23%, which is on the average 13 times greater than the observed change.

Furthermore, the hypothesis of a physical migration of bisulfate ion requires not merely that the bisulfate ion have a mobility some 200 times greater than that of other ions but also that it have a mobility many times greater than would be expected for any ion in a solvent so viscous as sulfuric acid. Walden[12] has shown that there is a fairly good inverse proportionality between the conductance of an ion and the viscosity of the solvent. On this basis it follows from the 27.6 to 1 ratio[13] of the viscosities of sulfuric acid and water that the equivalent conductance of a bisulfate in sulfuric acid should be in the neighborhood of 5.5 r. o., whereas the actual conductance is approximately 65 r. o.[3]

Some 99% of the conductance of a solution of a bisulfate in sulfuric acid depends therefore upon a process other than simple ionic migration. Certainly a possible mechanism for this process, and in many ways a very probable one, is that of a transfer of hydrogen ions from sulfuric acid molecules to adjacent bisulfate ions, a proton jump. It accounts for Ohm's law and the observed proportionality between conductance and concentration by the reasonable assumption that the probability of a jump increases with increasing field strength and with increasing concentration of bisulfate ion. It represents a conduction by hydrogen ions without the existence of free hydrogen ions, and in such fashion that the conductance is increased by that very change, increase in bisulfate ion concentration, which would necessarily decrease the concentration of free protons if they were present. In marked contrast to the simple ionic migration of bisulfate ion, its operation would not entail a transfer of solvent molecules and the consequent changes in concentration, which we have just shown do not occur.

This limited Grotthus chain theory has again and again been suggested[14] as an explanation of the large apparent mobilities of hydrogen and hydroxyl ions in water, the most recent revival being that of Bernal and Fowler,[14f] who attribute the proton jump to the quantum mechanical tunnel effect. The evidence for its applicability in aqueous solutions has been decidedly indirect; if it does exist, its effects are blurred by the competing mechanism of simple ionic migration. The behavior of other solvents, especially of ammonia, has been cited[14g,h] as evidence against the theory, but an explanation has been offered by Latimer and Rodebush[14c] in terms of relative strength of proton binding by different solvents. The proton binding in sulfuric acid is of course very weak, and the geometrical configuration of the molecule is also favorable to the mechanism. Furthermore, the high viscosity of sulfuric acid almost completely submerges the competition of simple ionic migration, and thus permits the most direct and conclusive evidence so far obtained of the operation of some other effect.

Summary

A small but real migration of barium ion in barium bisulfate solutions in the solvent sulfuric acid has been demonstrated.

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(10) This is true only of the measurements of Hantzsch, Ref. 3, at concentrations so large that the ionization of the solvent has been practically suppressed. There are indications that the results at lower concentrations of Bergius, *Z. physik. Chem.*, **72**, 338 (1910), are seriously complicated by changes in viscosity with concentration.

(11) The errors resulting from the inward migration of barium ion and the use of part of the current in solvent reduction at the cathode instead of hydrogen evolution are either negligible or would produce an even greater loss of solvent, for instance by the evaporation of sulfur dioxide formed by reduction of the solvent.

(12) Walden, "Salts, Acids and Bases," McGraw-Hill Book Co., Inc., New York, 1929, pp. 276 ff.

(13) (a) "Int. Crit. Tables," Vol. V, p. 10; (b) Dunstan and Wilson, *J. Chem. Soc.*, **91**, 83 (1907); *Proc. Chem. Soc.*, **30**, 104 (1914).

(14) (a) Danneel, *Z. Elektrochem.*, **11**, 249 (1905); (b) Hantzsch and Caldwell, *Z. physik. Chem.*, **58**, 575 (1907); (c) Latimer and Rodebush, THIS JOURNAL, **42**, 1432 (1920); (d) Hückel, *Z. Elektrochem.*, **34**, 546 (1928); (e) Huggins, THIS JOURNAL, **53**, 3190 (1931); (f) Bernal and Fowler, *J. Chem. Physics*, **1**, 515 (1933); *Trans. Faraday Soc.*, **29**, 1049 (1933). See also (g) Walden, *Z. Elektrochem.*, **26**, 72 (1920); (h) Kraus, "The Properties of Electrically Conducting Systems," The Chemical Catalog Co., Inc., New York, 1922, p. 206.

The apparent transference number of barium ion in these solutions is 0.012; by using the non-electrolyte trichloroacetic acid as reference solute, the true transference number has been shown to be about one-half of this.

It has been demonstrated that the process of conduction in these solutions cannot depend upon a simple ionic migration. This conclusion strongly supports the theory of conduction by intermolecular proton jumps which has been much discussed as an explanation of the anomalous mobilities of hydrogen and hydroxyl ions in aqueous solutions.

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[CONTRIBUTION FROM THE GAYLEY CHEMICAL LABORATORY OF LAFAYETTE COLLEGE]

The Fluidity of Anisole

BY JOHN A. GEDDES AND EUGENE C. BINGHAM

I. Introduction

In a recent investigation of the temperature coefficient of conductance of salts in anisole,[1] it was necessary to obtain the fluidity of the solvent as a function of temperature. This was calculated by one of the authors according to Bingham's method,[2] using the atomic temperature constants of Bingham and Spooner, and an association factor of 1.25, derived from considerations based on the theory of protection. It is the purpose of this paper to present the experimental determinations of the fluidity and association of anisole, and to compare the association with the previously predicted values.

II. Experimental

Measurements were made in a Bingham viscometer number 1–34, the apparatus being essentially that previously described by the authors.[3]

Anisole was purified by the method of Bien, Kraus and Fuoss,[1] and was distilled into the viscometer directly before use.

Densities for use in the kinetic energy correction term were calculated from Bien's empirical formula.

TABLE I

THE VISCOSITY AND FLUIDITY OF ANISOLE AT DIFFERENT TEMPERATURES

t, °C.	η, centipoises		φ, rhes
2.00	1.5082	1.5083	66.30
10.00	1.2931	1.2923	77.36
20.00	1.0863	1.0858	92.08
30.00	0.9280	0.9280	107.76
40.00	.8047	.8048	124.26
60.00	.6274	.6278	159.34
80.00	.5064	.5066	197.43
100.00	.4190	.4192	238.63

The experimental results are given in Table I, in which left and right limb determinations of η are given. It is observed that the maximum deviation is only 0.07%.

III. Discussion

The relationship between the fluidity of anisole and the temperature in degrees absolute is expressed over the range covered by the equation

$$0.7093\,\varphi = (T^2 - 562.95\,T + 104{,}632)^{1/2} + T - 387.5 \quad (1)$$

From this, the absolute temperatures actually required for fluidities of 50, 100, and 200 rhes can be obtained. These are listed in Table II, together with the values calculated from the atomic temperature constants, and the association "n." (n = observed absolute temperature/calculated absolute temperature.) Extrapolated values are given in parentheses.

TABLE II

ASSOCIATION OF ANISOLE BY FLUIDITY METHOD

Fluidity in rhes	Absolute temperature Obs.	Absolute temperature Calcd.	Association "n"
50	(262.4)	209.9	(1.250)
100	298.2	239.8	1.244
200	354.2	282.3	1.255

It is seen that the observed associations agree remarkably well with the predicted value of 1.25. No definite value for the association effect upon introducing an OCH_3 group into a compound had been determined, which may account for the very slight discrepancy noted. It is found to be a mildly protective group, being just below H in the scale.[3]

Summary

The fluidity of anisole has been measured over the temperature range 2–100°, and represented by a formula of the usual type.

Experimentally determined values of the as-

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[1] Bien, Kraus and Fuoss, THIS JOURNAL, **56**, 1860 (1934).

[2] Bingham and Spooner, *J. Rheology*, **3**, 221 (1932); *Physics*, **4**, 387 (1933).

[3] Bingham and Geddes, *Physics*, **4**, 203 (1933); **5**, 42 (1934).