cules. In view of the weakness of the radiation, this conclusion may have only minor significance even though the flame itself is observed on this account. There is evidence[15] that the eye is sensitive to as little as 10^{-9} erg per second in the blue-green, corresponding to about 200 quanta per second. Since about 10^{18} molecules are reacting per second, only a vanishingly small fraction of elementary processes result in radiation.

(15) Wentworth, *Psychological Monographs*, **40**, pp. 136, etc. (1930).

Summary

The cool flame region in 1:1 propane–oxygen mixtures is not materially affected by etching the reaction tube or coating it with potassium chloride. It is thus determined by conditions in the gas phase. Attention is drawn to the region of negative temperature coefficient of the rate as an effective control, leading to successive flames and preventing ignition.

PRINCETON, NEW JERSEY RECEIVED JANUARY 20, 1940

[CONTRIBUTION FROM METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXII. Conductance of Ethylene Dichloride Solutions of Some Quaternary Ammonium Salts Having Large Negative Ions[1]

BY D. LEIGH FOWLER AND CHARLES A. KRAUS

In earlier papers of the present series, the behavior of solutions of electrolytes in different solvents has been sketched in broad outline. It has been shown that the properties of dilute solutions of typical electrolytes are accounted for rather satisfactorily through a combination of the ion-atmosphere theory of Debye and Hückel and Onsager with the ion-association theory of Bjerrum. The properties of dilute electrolyte solutions are dependent upon the temperature, the dielectric constant and the viscosity of the solvent medium and the size of the ions. In order to elucidate more fully the phenomena characteristic of electrolytic solutions, further knowledge is required concerning specific factors such as the constitution and configuration of the ions and their interactions with one another and with the solvent molecules. In certain cases, interactions between the ions and polar molecules other than those of the solvent are also of interest.

The present paper is the first of a series dealing with the conductance of various types of electrolytes when dissolved in ethylene dichloride, pyridine and nitrobenzene. The dielectric constants of these solvents are 10.23,[1a] 12.01[2] and 34.50,[3] respectively. None of these solvents has an active hydrogen atom and only pyridine has pronounced basic properties. All these solvents permit of accurate determination of Λ_0 values.

The present paper is primarily concerned with the determination of ion conductances in ethylene dichloride. In this, as in most nonaqueous solvents, reliable transference measurements cannot be made. Accordingly, it is necessary to resort to other means for approximating limiting ion conductances. It is well known that the mobility of ions, containing a large number of carbon atoms, decreases with increasing number of such atoms and that the decrease per atom decreases as the number of atoms increases. By introducing a large, and approximately equal, number of carbon atoms into the two ions of an electrolyte, these ions will have very nearly the same mobility and, accordingly, the limiting conductance of each ion will be one-half that of the electrolyte. Combining these ions with other ions and determining the Λ_0 values, the conductance of other ions may be approximated.

In an earlier paper,[4] it was shown that the fluoride and hydroxyl ions form stable complexes with triphenylboron and several quaternary ammonium salts of these ions have been described. To determine the ion conductance, we have measured the conductance of solutions of tetrabutylammonium triphenylborofluoride and tetrabutylammonium triphenylborohydroxide. We have also measured the conductance of several tetramethylammonium salts of the same ions.

II. Experimental

Solvent.—For the present investigation, ethylene dichloride was employed as a solvent. The method of puri-

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[1] This paper is based on a portion of a thesis presented by D. L. Fowler in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, 1935.

(1a) G. S. Hooper, Thesis, Brown University, 1933.

(2) Le Fèvre, *J. Chem. Soc.*, 776 (1936).

(3) Lattey and Gattey, *Phil. Mag.*, **7**, 985 (1929).

(4) Fowler and Kraus, THIS JOURNAL, **62**, 1143 (1940).

fication was essentially that of Mead[5] and the solvent employed had a specific conductance of 2×10^{-11} or less.

Electrolytes.—The electrolytes studied were tetra-*n*-butylammonium triphenylborohydroxide, tetra-*n*-butylammonium triphenylborofluoride, tetramethylammonium triphenylborohydroxide monohydrate, tetramethylammonium triphenylborohydroxide monoalcoholate and tetramethylammonium triphenylborofluoride. The preparation of these salts already has been described.[4]

Experimental Procedure.—The method employed in carrying out the measurements was practically the same as that of Mead[5] and need not be described in detail here. This applies to the setup of electrical apparatus as well as to the types of cells employed and the method of carrying out the dilutions.

Constants.—All measurements were carried out at 25 ± 0.01° with thermostatic regulation good to 0.002°. Cell constants were obtained by comparison with a standard cell which, in turn, was calibrated with a 0.1 demal solution of potassium chloride at 25°, using the conductance values of Jones and Bradshaw.[6] The constants of the cells used were 0.10662, 0.21255 and 0.10670. In the computations, the density of the solvent was taken to be 1.2455 at 25.00°, as determined by Bien.[7] Since all solutions were dilute, the density of the solution was assumed equal to that of the solvent. All weighings, both those of solvent and of solute, were made in air; since the two have approximately the same density, it was unnecessary to convert to weights *in vacuo*. In the computations, the dielectric constant has been assumed to be 10.23 and the viscosity 0.00785.

III. Results

The experimental results are given in Table I in which the concentration in moles of salt per liter of solution appears in the first column and the equivalent conductance in the second column. Two independent series of measurements were carried out in all cases with an agreement of the order of 0.2%, or better. Data for only one series of measurements are given, excepting for tetra-*n*-butylammonium triphenylborohydroxide and tetra-*n*-butylammonium triphenylborofluoride, whose values were intended to be used in determining the limiting ion conductance values upon which ion conductances of other salts are to be based.

TABLE I

CONDUCTANCE OF DIFFERENT SALTS IN ETHYLENE DICHLORIDE AT 25°

$C \times 10^4$	Λ	$C \times 10^4$	Λ
Series 1		Series 2	
A. $(C_4H_9)_4NOH\cdot B(C_6H_5)_3$			
11.66	23.61	11.40	23.75
5.798	28.17	6.413	27.50
3.275	32.16	3.497	31.73
1.831	36.22	1.957	35.79
0.9977	40.15	1.046	39.89
.5578	43.40	0.5746	43.30
.2856	46.37	.2782	46.55
.1675	48.12	.1440	48.66
B. $(C_4H_9)_4NF\cdot B(C_6H_5)_3$			
Series 1		Series 2	
14.49	20.58	16.24	19.77
7.102	25.07	7.982	24.12
3.198	30.69	3.730	29.41
1.615	35.61	1.884	34.37
0.8356	39.94	1.009	38.69
.4193	43.89	0.4754	43.21
.2133	46.82	0.2495	46.23
C. $(CH_3)_4NF\cdot B(C_6H_5)_3$		D. $(CH_3)_4NOH\cdot B(C_6H_5)_3\cdot C_2H_5OH$	
11.83	10.32	8.759	11.69
6.928	12.75	5.112	14.37
3.616	16.45	3.181	17.25
1.878	21.12	1.457	23.15
1.015	26.41	0.9182	27.31
0.4862	33.74	0.3562	37.12
0.2843	39.58		
E. $(CH_3)_4NOH\cdot B(C_6H_5)_3\cdot H_2O$			
13.43	9.64		
7.458	12.16		
4.011	15.56		
1.930	20.67		
0.8723	27.68		
.4436	34.69		
.2326	41.91		

IV. Discussion

The data have been treated graphically by the method of Fuoss,[8] plotting values of F/Λ against values of $c\Lambda f^2/F$. The plots are shown in Fig. 1 and embrace all series including those omitted for three of the salts. As may be seen upon inspection of the figure, the experimental points lie upon straight lines in accord with the requirements of the theory which takes into account ionic association as well as ion atmosphere effects. On extrapolating the curves to the axis of ordinates, values of $1/\Lambda_0$ are obtained while the slope of the curves is proportional to $1/K\Lambda_0^2$. Therefore, values of both Λ_0 and K may be conveniently derived from the plots. These values are given in Table II.

TABLE II

CONSTANTS OF ELECTROLYTES IN ETHYLENE DICHLORIDE AT 25°

Salt	Λ_0	$K \times 10^4$
$(C_4H_9)_4NOH\cdot B(C_6H_5)_3$	52.3	2.63
$(C_4H_9)_4NF\cdot B(C_6H_5)_3$	52.4	2.03
$(CH_3)_4NF\cdot B(C_6H_5)_3$	68.5	0.201
$(CH_3)_4NOH\cdot B(C_6H_5)_3\cdot C_2H_5OH$	68.5	.202
$(CH_3)_4NOH\cdot B(C_6H_5)_3\cdot H_2O$	70.5	.186

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

[6] Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

[7] G. S. Bien, Thesis, Brown University, 1934.

[8] Fuoss, THIS JOURNAL, **57**, 488 (1935).

In accord with earlier observations, salts with larger ions have lower conductances and higher dissociation constants. Comparing the tetrabutylammonium and the tetramethylammonium triphenylborofluoride salts, the conductance of the tetramethyl ion is 16.2 units higher than that of the tetrabutylammonium ion. This is in fairly good accord with the values determined by Mead[5] with the picrates where the difference found is 16.4. Mead's values for the picrates are probably somewhat more reliable than are the present values for the triphenylborofluoride salts which are purified with rather greater difficulty than are the picrates.

The conductance values for tetrabutylammonium triphenylborohydroxide and tetrabutylammonium triphenylborofluoride are practically identical, namely, 52.3 and 52.4. If we assume that the two ions have equal mobilities, then the ion conductances will be 26.2. This yields a value of 42.3 for the tetramethylammonium ion. It is interesting to note that the conductance values for tetramethylammonium triphenylborofluoride and tetramethylammonium triphenylborohydroxide monoalcoholate are identical, – 68.5. On the other hand, that of the corresponding monohydrate is distinctly higher. It is not believed that the difference is due to impurities, since the alcoholate and the hydrate are readily interconvertible and there is no reason for believing that one salt was less pure than the other.

As a standard wherewith to fix ion conductances, tetrabutylammonium triphenylborofluoride is much more satisfactory than is the corresponding triphenylborohydroxide because it is decidedly more stable and is more readily purified. A sample of the original borohydroxide which was used in the present investigation was recently remeasured by Mr. W. E. Thompson and, while the Λ_0 value coincided with the present one, the conductances at higher concentration were markedly higher than those here recorded. For example, at a concentration of 2×10^{-4}, the conductance value found was 5% above the present value. Upon recrystallization, the difference was reduced to 2.5%. In the case of an original sample of tetrabutylammonium triphenylborofluoride, the conductance on measuring at 4×10^{-4} was found to be 1% above the value here recorded and at 1×10^{-4} the value was 0.25% higher. Upon several recrystallizations from absolute alcohol, however, the fluoride yielded values checking those here recorded.

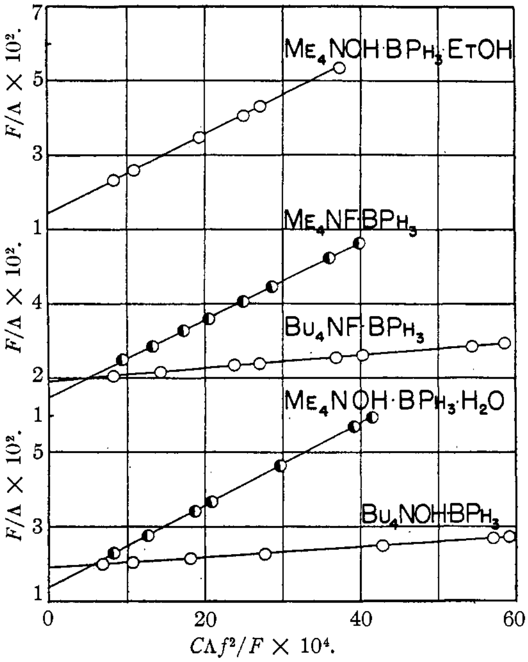

Fig. 1.—Plots of conductance function for electrolytes in ethylene chloride at 25°.

As may be seen from the table, the K values for the tetramethylammonium salts are approximately one-tenth those of the corresponding tetrabutylammonium salts; this is in accord with the ion association theory. Computations of the distance between centers of charge[9] give values of approximately 3.9×10^{-8} for the tetramethyl salts and 5.6 and 5.9, respectively, for the tetrabutylammonium triphenylborofluoride and triphenylborohydroxide. These values seem reasonable enough but, as will be shown in later papers of this series, there are electrolytic systems which yield values that are unduly high or unduly low.

V. Summary

1. The conductance of the following salts has been measured in ethylene dichloride solution at 25.00°: $(n\text{-}C_4H_9)_4NOH \cdot B(C_6H_5)_3$, $(n\text{-}C_4H_9)_4NF \cdot B(C_6H_5)_3$, $(CH_3)_4NOH \cdot B(C_6H_5)_3 \cdot C_2H_5OH$, $(CH_3)_4NOH \cdot B(C_6H_5)_3 \cdot H_2O$ and $(CH_3)_4NF \cdot B(C_6H_5)_3$.

2. The Λ_0 values for the two tetrabutylammonium salts were found to be practically identical—52.3 and 52.4. Assuming the tetrabutylammonium ion and the triphenylborofluoride ion (or the corresponding hydroxy ion) to have the same mobility, the conductance of each of the two ions is 26.2. The complex fluoride was found

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(9) Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

to be more stable than the corresponding hydroxide.

3. Dissociation constants of the ion–ion pair equilibrium have been computed. Salts with larger ions have larger dissociation constants.

PROVIDENCE, RHODE ISLAND RECEIVED JUNE 24, 1940

NOTES

The Sulfites of Aluminum and Iron at 30°

BY WARREN F. BARTZ

Studies of the reactions of the oxides of aluminum and of iron, respectively, with aqueous sulfur dioxide have led to many publications including patents. Several sulfites of each base have been described and it would appear that high concentrations of the metals are attained in the liquid phase. This communication reports observations on the composition of the solids formed when sulfur dioxide is injected into aqueous suspensions of the hydroxides at 30°.

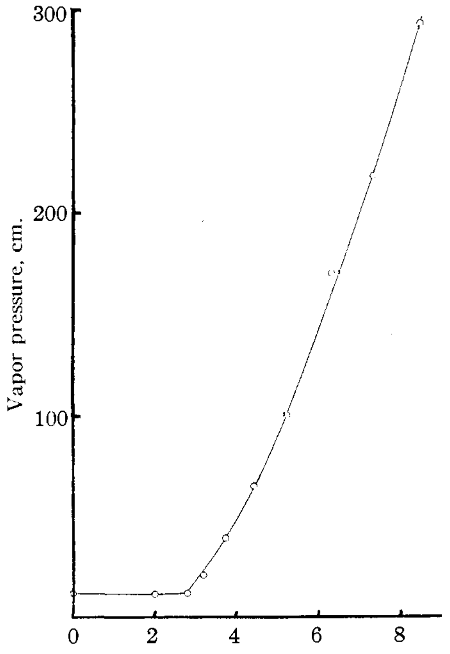

Fig. 1.—Vapor pressures in the system H_2O–SO_2–Al_2O_3.

Aluminum hydroxide was prepared by precipitation with ammonia from a solution of aluminum chloride and washing the precipitates free from chlorides. The dried precipitate with about an equal weight of water was placed in a glass absorption vessel which was attached to a manometer by a flexible copper tube, so the vessel could be agitated in a constant temperature-bath. The bath was kept at 30 ± 0.1°. Air was removed by suction and flushing with a small amount of sulfur dioxide. Measured quantities of sulfur dioxide were then introduced and the resulting pressures observed. At a pressure of about 300 cm. the process was reversed and measured amounts of sulfur dioxide withdrawn and pressures noted. Alternating the addition and withdrawal of sulfur dioxide led finally to sets of observations which all fell on a graph as shown in Fig. 1. It was not considered desirable to attain higher pressures since there was no indication that another metal sulfite would be found. The formation of the well-known hydrate of sulfur dioxide was not desired. It appeared that but one sulfite of aluminum is formed at 30°, and further additions of sulfur dioxide merely ran the vapor pressure of the suspension proportionally to the excess of added gas. Analysis of the solid formed in the absorption vessel leads to the formula $Al_2O_3 \cdot 1.86SO_2 \cdot 5.9H_2O$, while a product obtained by bubbling sulfur dioxide through a suspension for a month and then storing over sulfuric acid for two months leads to the formula $Al_2O_3 \cdot 2.03SO_2 \cdot 6.7H_2O$. It may be concluded that the product is the basic sulfite $Al_2O_3 \cdot 2SO_2 \cdot 6H_2O$. This agrees with the results obtained by Huber,[1] but Rosencranz and Hüttig[2] report but 3.3 water in the product obtained by them.

The colorless product is quite stable in dry air. Heated in a dilatometer with cottonseed oil, it was stable to 105° when it decomposed rapidly and was not reformed on cooling. The sulfite dissolves in water, but slowly, even in the presence of an excess of sulfur dioxide. Unless air be rigor-

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[1] K. Huber, *Helv. Chim. Acta*, **18**, 858 (1935).

[2] E. Rosencranz and G. Hüttig, *Gazz. chim. ital.*, **14**, 360 (1884).