at 40°, and with constant stirring these solutions were brought to equilibrium at 25°. Known volumes were evaporated to dryness at 70°, weighed and then kept over P_2O_5 for several days and reweighed. In addition two saturated solutions for each salt were prepared below 20° and brought to equilibrium at 25° and then treated as above. All solutions were handled in polyethylene ware. Spectrographic analyses of these salts showed no or only minor traces of impurities. The solubilities are listed in Table III.

TABLE III

SOLUBILITIES OF THE HEXAFLUOROCOMPLEXES AT 25°

Compound	Solution, mole/l.
K_2SiF_6	0.00572
Rb_2SiF_6	.00690
Ce_2SiF_6	.0234
K_2GeF_6	.0221
Rb_2GeF_6	.0167
Ce_2GeF_6	.0471
K_2SnF_6	.128
Rb_2SnF_6	.0615
Ce_2SnF_6	.0792
K_2TiF_6	.0595
Rb_2TiF_5	.0248
Cs_2TiF_6	.0551
K_2ZrF_6	.0812
Rb_2ZrF_6	.0848
Cs_2ZrF_6	.112
K_2HfF_6	.128
Rb_2HfF_6	.186
Cs_2HfF_6	.174

Acknowledgment.—The spectrographic analysis of the salts prepared for this research was performed by Mr. Ellis Creitz of the United States Bureau of Mines.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, SOUTH CAROLINA]

The Conductance of Tetra-*n*-butylammonium Picrate in Benzene–*o*-dichlorobenzene Solvent Mixtures at 25°

BY W. R. GILKERSON AND R. E. STAMM

RECEIVED MARCH 7, 1960

The conductance of tetra-*n*-butylammonium picrate as a function of concentration has been determined in 75, 50, 25, 10 and 0 mole % *o*-dichlorobenzene and benzene solvent mixtures at 25°. The ion pair dissociation constant *K* and limiting equivalent conductance have been obtained. The latter does not follow Walden's rule. From the slope of a log *K versus* reciprocal dielectric constant plot, a distance of closest approach, *a*, of 6.64 Å. was obtained.

The exact dependence of the ion pair dissociation constant *K* for the process in solution upon di-

$$AB \rightleftharpoons A^+ + B^-$$

electric constant, temperature, nature of the solvent and nature of the salt has been the subject of considerable recent discussion.[1-5] In order to pinpoint the various factors which affect the pairing process a wide variety of systems must be studied. Fuoss and co-workers (see ref. 5) are investigating salts in polar–nonpolar solvent mixtures in the dielectric range 20 to 78.5. Stern and co-workers are studying salts in pure solvents in the low dielectric range of 10 to 5 (ref. 3). We report here an examination of the pairing of tetra-*n*-butylammonium picrate in benzene–*o*-dichlorobenzene (*o*-DCB) mixtures as solvent. This system ranges in dielectric constant from 2.275 to 10.0 (see Table I). The salt chosen is soluble enough over the entire range of solvent composition. Since the dipole moment of *o*-DCB is 2.5 debyes,[6] while benzene has no moment, we might expect preferential solvation by the former if dipole–ion interaction is the predominant feature of this effect. Further, the salt chosen has been examined in pure *o*-DCB by several workers.[3,7,8] The values of the dissociation constant *K* and the limiting equivalent conductance Λ_0 are in good agreement at 25°.

Experimental

Solvents.—Benzene (Merck reagent grade) was recrystallized, passed through a 35 × 2 cm. column packed with Alcoa activated alumina, grade F-20, refluxed over sodium ribbon for 30 minutes and distilled on a three foot packed column, b.p. 80.1°. The middle cut was again passed through an alumina column prior to use. The specific conductance of the pure benzene was 4×10^{-13} ohms^{-1} cm.$^{-1}$.

o-DCB (Eastman red label) was passed through the alumina column and distilled at 10 mm., b.p. 62°. The middle cut was passed through the alumina column prior to use. The specific conductance of the *o*-DCB was 1.3×10^{-9} ohms^{-1} cm.$^{-1}$. Solvent mixtures were made up by weight.

Salt.—The tetra-*n*-butylammonium picrate was prepared as described previously (ref. 4). Solutions were prepared in a nitrogen-filled drybox.

Cells.—Two of these were of the Kraus type, having cell constants of 0.03000 and 0.01800 as determined by intercomparison with a 0.01D KCl solution.[9] The third cell was originally designed[10] as a capacitance cell but has been used here to determine the conductance of the most dilute benzene solutions. The air capacity of the cell was determined to be 24.57 pf., using benzene as a standard. The cell constant, for conductance purposes, was found to be 0.00474 by comparison with one of the other cells.

Conductance Measurements.—Two bridges were used. For the lower resistances, the Leeds and Northrup bridge

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(1) J. T. Denison and J. B. Ramsey, THIS JOURNAL, **77**, 2615 (1955).

(2) R. M. Fuoss, *ibid.*, **80**, 5059 (1958).

(3) P. H. Flaherty and K. H. Stern, *ibid.*, **80**, 1034 (1958).

(4) W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

(5) H. Sadek and R. M. Fuoss, THIS JOURNAL, **81**, 4511 (1959).

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(7) F. Accascina, E. L. Swarts, P. L. Mercier and C. A. Kraus, *Proc. Natl. Acad. Sci. U. S.*, **39**, 917 (1953).

(8) H. L. Curry and W. R. Gilkerson, THIS JOURNAL, **79**, 4021 (1957).

(9) G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

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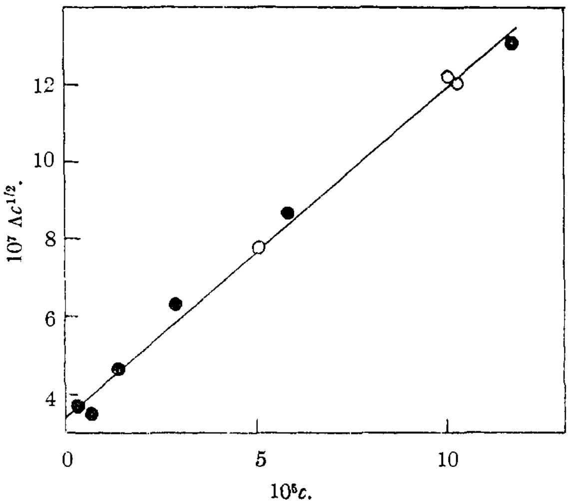

Fig. 1.—Bu_4NPi in benzene at 25°: ○, Kraus type cell; ●, capacitance cell.

and associated circuits previously described (ref. 8) was used. This had an upper limit of 10^8 ohms for 1% precision. For higher resistances a General Radio type 716-C Capacitance bridge, equipped with a type 716-P4 Guard Circuit, was used. This is a Schering bridge and provides a conductance (as dissipation factor) as well as capacitance balance. A resistance of 10^{10} ohms could be measured at 1 kc. with a precision of 10%. Use of such a bridge for this resistance range was suggested some time ago.[11] All measurements were made using an oil thermostat at 25.00°. In calculating the conductance of an unknown solution from substitution measurements using the type 716 bridge, it is necessary to multiply the bridge reading (dissipation factor) by the total capacitance in parallel with the solution resistance. All the parallel capacitance C' except that due to leads C'' was known. One is unable to obtain the lead capacitance in any way other than by measuring a known resistance. We included the ratio $(C' + C'')/C'$ in the cell constant. That is the reason the latter has the value 0.00474 rather than the theoretical one of 0.00360 (= 0.0885/24.57). The gold cell measurements were checked at frequencies of 10, 20, 50, and 100 kc. No change in conductance with frequency was noted.

Dielectric Constants.—The dielectric constants of the solvents were determined using the capacitance cell and bridge described above. The results are given in Table I. All dielectric measurements were made at 100 kc.

Viscosity and Density.—These were determined for each solvent mixture. The former was measured in a Cannon–Fenske viscometer. The results are listed in Table I.

TABLE I

DIELECTRIC CONSTANT, VISCOSITY AND DENSITY OF BENZENE-o-DICHLOROBENZENE MIXTURES AT 25°

Mole % o-DCB	D	$10^2\eta$, poises	d, g./ml.
0	2.274[a]	0.610	0.8734
10	3.039	.640	.9248
24.82	4.152	.690	.9978
50.03	6.041	.839	1.1110
74.81	7.946	1.038	1.2095
100	10.06[b]	1.278[c]	1.3007

[a] A. A. Maryott and E. R. Smith, Table of Dielectric Constants of Pure Liquids, N.B.S. Circular 514, August 10, 1951. [b] See ref. 12. [c] Ref. 8.

Results

The conductance data are given in Table II.

In 75 and 50 mole % DCB, the ion pair dissociation constant K and the limiting equivalent conductances Λ_0 were determined by the method of Shedlovsky.[13] The values are listed in Table III. The extrapolation to infinite dilution in the case of 50 mole % DCB was rather long. The uncertainty we attribute to this is listed in Table III.

TABLE II

EQUIVALENT CONDUCTANCE OF Bu_4NPi IN BENZENE-o-DICHLOROBENZENE SOLUTIONS AT 25⁰

0[a] Mole % DCB 10^5c, mole/l.	$10^1\Lambda$	10[a] Mole % DCB 10^4c, mole/l.	$10^3\Lambda$	24.82 Mole % DCB 10^4c, mole/l.	$10^2\Lambda$
10.24	1.19	10.14	2.578	11.95	3.96
10.00	1.22	5.039	2.362	5.230	4.80
5.09	1.09	2.325	2.444	2.722	5.99
11.7	1.21[b]	1.006	3.002	1.104	8.76
5.86	1.13[b]	0.500	3.923	0.5893	11.80
2.91	1.17[b]				
1.45	1.21[b]				
0.729	1.30[b]				
0.363	1.96[b]				

50.03 Mole % DCB		74.82 Mole % DCB	
10^4c, mole/l.	Λ	10^4c, mole/l.	Λ
10.04	0.6056	20.14	1.984
4.812	0.8084	9.979	2.572
2.509	1.089	5.024	3.418
0.997	1.660	2.524	4.426
0.5065	2.262	1.035	6.327
		0.4971	8.383

[a] Determined on General Radio Capacitance bridge. [b] Determined using cell 3, the gold plated capacitance cell.

In the case of 25, 10 and 0 mole % DCB, the conductance data were treated by the method of Fuoss and Kraus[14] to obtain the product $\Lambda_0 K^{1/2}$. A plot of $\Lambda c^{1/2}$ versus c for benzene is shown in Fig. 1. It was not possible to determine Λ_0 in these solvent systems. It is customary in such a case to assume that the Walden product $\Lambda_0\eta_0$ is a constant, and from knowledge of Λ_0 in a higher dielectric solvent, to then estimate Λ_0 in the lower dielectric case. However, note the values of $\Lambda_0\eta_0$ obtained in the 75 and 50 mole % DCB. For

TABLE III

Λ_0 AND K FOR Bu_4NPi IN BENZENE–DCB SOLVENT MIXTURES AT 25°

Solvent, mole % DCB	Λ_0 I[a]	Λ_0 II[b]	K I[a]	K II[b]
0	77	77	1.84×10^{-17}	
10.00	73.5	62.5	1.84×10^{-13}	2.54×10^{-13}
24.83	68	47	1.69×10^{-10}	3.54×10^{-10}
50.03	56	30 ± 3	0.85×10^{-7}	2.74×10^{-7}
74.82		25		7.25×10^{-6}
100[c]		36.8		1.92×10^{-5}

[a] Λ_0 calculated from Walden product. [b] Λ_0 obtained by extrapolation by the Shedlovsky method for 75 and 50 mole % DCB systems. The values for 25 and 10 mole % DCB were read off the graph of Λ_0 *versus* mole fraction DCB. [c] Ref. 8.

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(11) W. F. Luder, P. B. Kraus, C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **58**, 255 (1936).

(12) Stern and Flaherty (ref. 3) reported this value from measurements made at the National Bureau of Standards. We had previously reported (ref. 8) 9.94 for this solvent at 25°. The differences have been found to be due to our neglect of a small amount of lead capacitance (0.16 pf.) in the cell. We originally thought that this was completely balanced out by using the guard electrode. Recalculation of our data shows agreement with the Bureau of Standards values within 0.2%.

(13) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(14) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 2387 (1933).

these two systems we find values of 0.260 and 0.252 respectively. These are to be compared to a value of 0.470 in pure DCB (ref. 8). There has been a drastic reduction in the Walden product as soon as benzene is added to DCB. We asume that Λ_0 in benzene can be calculated from the Walden product in pure DCB. A plot of Λ_0 (observed) for the 100, 75 and 50 mole % DCB systems as well as that calculated for benzene was made. For the 10 and 25 mole % DCB mixtures, we feel that Λ_0 read off the graph (and shown in Table III) are probably closer to the actual values of Λ_0 in these mixtures than those calculated from the Walden product. The former were used to calculate the values of the dissociation constant K appearing in Table III.

Discussion

We think the explanation for the behavior of Λ_0 has already been proposed by Fuoss[15] who pointed out the decrease in the Walden product as the dielectric constant decreased for a number of systems. He deduced that oriented solvating dipoles, left behind as the ion moves under the influence of the external field, would produce a drag effect, resulting in an increase in the local viscosity. There should be no such effect in benzene.

A plot of $-\log K$ *versus* $1/D$ for tetra-*n*-butylammonium picrate in the present solvent mixtures was made. The points fell surprisingly close to a straight line, with the exception of pure DCB. The addition of benzene to DCB decreases the dielectric constant and the ion pair dissociation constant but does not lower the latter as much as one would expect, if all the effect were due to the change in dielectric constant.

It is apparent that unless one allows changes in the distance of closest approach, a, the equation of Denison and Ramsey (ref. 1), which we shall call K_1, cannot apply to our data. They give

$$K_1 = \exp(-e^2/DakT) \qquad (1)$$

where e is the ion charge and a the distance of closest approach. Without varying a, this equation cannot account for the nonlinearity between 100 and 75% DCB. Fuoss (ref. 2) has arrived at the expression

$$K = (3000/4\pi Na^3)\exp(-e^2/DakT) \qquad (2)$$

Fuoss assumed that the ions in the ion pair were identical to the free ions, except for the electrostatic energy of interaction opposing motion in an external field. One of us (ref. 4) assumed that the ion pair behaved as a unit as far as translational motion was concerned and using free volume partition functions for the species present, obtained

$$K = (2\pi\mu kT/h^2)^{3/2}(gv\sigma)\exp(-E_s/RT)\exp(-e^2/DakT) \qquad (3)$$

where all the quantities are defined in the original paper. An error is present in eq. 3 because K in this equation is the dissociation constant on the mole fraction scale. This is also the case for eq. 1. However, the dissociation constants are usually reported on the molarity scale. In the dilute solutions one is usually concerned with, both eq. 1 and 3 should be multiplied by the factor $1000d/M$, where d is the solvent density and M its molecular weight, or the mean molecular weight of a mixture. Now, it might be pointed out that if the same model is used in the derivation of eq. 3 as was used by Fuoss, then the final result on the molarity scale is

$$K = \frac{1000d}{M}(v^+v^-/v_+{}'v_-{}')\exp(-E_s/RT)\exp(-e^2/DakT) \qquad (4)$$

where the v's are the free volumes available to the ions, and the primed values refer to those in the ion pair itself. Fuoss in a later paper (ref. 5) has included the factor containing the solvation term E_s in his expression so that we may now write it as

$$K = (3000/4\pi Na^3)\exp(-E_s/RT)\exp(-e^2/DakT) \qquad (5)$$

The two equations 4 and 5 are practically identical. We will now compare our data with a relation of the form of (4) or (5).

Our original inference, that *o*-dichlorobenzene would preferentially solvate the ions, does not seem borne out in fact. A clue may be the early report[16] confirmed by us that as benzene is added to a picrate salt, a concentrated solution occurs. As more benzene is added, two liquid phases form, one being very rich in salt. These two phases do not coalesce until quite an excess of benzene has been added. No quantitative data are available on this point. But apparently benzene does solvate picrate salts (ions or clumps?) quite extensively. Whatever we can ascribe it to, we can say that the dielectric independent term E_s in eq. 4 and 5 is constant as the DCB concentration decreases beyond 75 mole %. For the straight line portion of the log K *versus* $1/D$ plot we can calculate an apparent a of 6.64 Å.

It is difficult to reconcile the a values so obtained with the distance between charges calculated from dipole moment measurements on this salt in benzene.[17] The latter yielded a distance of 3.73 Å. Fuoss and Kraus[18] report an a value of 5.55 Å. for tetra-*n*-butylammonium iodide in dioxane–water mixtures at 25°. The bromide has an a value of 5.36 Å. in nitrobenzene–carbon tetrachloride mixtures (ref. 5) at 25°. Using the crystallographic radii for bromide and iodide ions, we find a radius for the tetra-*n*-butylammonium ion of 3.41 and 3.38 Å., respectively, in these two cases, assuming that the distance of closest approach is the sum of the ionic radii. We then calculate that the picrate ion, from the present data, has an effective radius of 3.3 Å. From a model of the picrate ion, the radius along the phenolic oxygen–*p*-nitro group axis is 4.3 Å. Thus, the charge may be said to reside about one ångström from the center, toward the phenolic oxygen. This is not completely unreasonable. We suggest the possibility that a reëxamination of the dipole moments of ion pairs in benzene at concentrations below $10^{-4}M$ may result in larger values, in better

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[15] R. M. Fuoss, *Proc. Natl. Acad. Sci. U. S.*, **45**, 807 (1959).

[16] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 3614 (1933).

[17] J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **180**, 585 (1936).

[18] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **79**, 3304 (1957).

agreement with those obtained from the variation of dissociation constant with dielectric constant in solvent mixtures.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, B. C., CANADA]

Some Salts of Trifluoromethylfluoroboric Acid[1,2]

BY R. D. CHAMBERS, H. C. CLARK AND C. J. WILLIS

RECEIVED MARCH 29, 1960

Trimethyltrifluoromethyltin reacts with boron trifluoride to give a 1:1 adduct, formulated as trimethyltin trifluoromethylfluoroborate, $(CH_3)_3Sn^+$, $[CF_3BF_3]^-$. The potassium, barium and ammonium salts of the hypothetical trifluoromethylfluoroboric acid HBF_3CF_3 are prepared from this adduct. The stability of the ion $[CF_3BF_3]^-$ is attributed to the saturation of the acceptor tendencies of the boron atom and the delocalization of the charge on the ion.

We have previously described the preparation of trimethyltrifluoromethyltin by the reaction of hexamethylditin with trifluoroiodomethane[3,4]

$$(CH_3)_3Sn\text{–}Sn(CH_3)_3 + CF_3I \longrightarrow (CH_3)_3SnCF_3 + (CH_3)_3SnI$$

Differences in behavior between this compound and analogous known perfluoroalkyl compounds of other elements were ascribed to the electropositive nature of the tin atom, leading to polarization of the $Sn\text{–}CF_3$ bond. It was therefore of interest to investigate the reaction of trimethyltrifluoromethyltin with strong electron acceptor molecules, in the hope of inducing complete heterolytic fission of the $Sn\text{–}CF_3$ bond and the production of complex salts containing the trimethyltin cation. Other workers[5] have reported that alkyl-perfluoroalkyl tin compounds release alkyl rather than perfluoroalkyl groups on treatment with electrophilic reagents (H^+ or BCl_3, etc.) and described this result as surprising.

We have now found that trimethyltrifluoromethyltin reacts readily with boron trifluoride to form a 1:1 adduct, whose properties clearly indicate that it should be formulated as trimethyltin trifluoromethylfluoroborate, $(CH_3)_3Sn^+$ $[CF_3BF_3]^-$.

When a mixture of trimethyltrifluoromethyltin and boron trifluoride was allowed to warm up from −196 to 20°, a reaction occurred rapidly with the production of solid material, but considerable darkening was also noticed and a pure product could not be isolated. It was found, however, that reaction in carbon tetrachloride solution immediately precipitated the insoluble white adduct; recovery of excess boron trifluoride showed that equimolar quantities had reacted. The complex was extremely hygroscopic and was handled in a dry atmosphere. On keeping it slowly decomposed, darkening in color and evolving boron trifluoride.

The analogous phosphorus compound $(CH_3)_2PCF_3$ also forms with boron trifluoride a 1:1 adduct, which has been formulated as a simple molecular addition compound involving donation from the phosphorus to the boron atom.[6] Such coördination must be considered very unlikely for trimethyltrifluoromethyltin, however, since no electrons are available on the tin atom for donation.

The formation of an adduct with an ionic structure would occur by removal of the trifluoromethyl group from the tin atom as CF_3^-, giving the familiar trimethyltin cation and the trifluoromethylfluoroborate anion $[CF_3BF_3]^-$. This is the first example to be reported of such transfer of a trifluoromethyl group and demonstrates clearly the pseudo-halogen character of this group. Complex anions derived from the perfluoroalkyl mercurials are known,[7] such as $[(CF_3)_2HgI_2]^=$, but these are formed by transfer of a halide ion rather than a trifluoromethyl group. The heterolytic fission of the $Sn\text{–}CF_3$ bond will be facilitated by the electropositive nature of the tin atom and in particular by the stability of the trimethyltin cation. It seems probable, therefore, that similar reactions may occur between acceptor molecules and perfluoroalkyl derivatives of other electropositive elements, such as lithium, magnesium and zinc; this is being investigated.

The trifluoromethylfluoroborate anion has not been reported previously; indeed no stable compound containing a trifluoromethyl-boron linkage is known despite much work in this field. Because of the strong acceptor properties of boron, it has been suggested[8] that simple perfluoroalkyl derivatives of trivalent boron would be unstable, and this is supported by the reported decomposition of the compound $CF_2{:}CFBCl_2$ to give boron trifluoride.[5] In the trifluoromethylfluoroborate ion, however, the acceptor properties of the boron atom are fully satisfied, conferring stability on the ion.

Trimethyltin trifluoromethylfluoroborate is freely soluble in water, giving a stable solution, and this property was used to prepare other salts of the hypothetical trifluoromethylfluoroboric acid HBF_3CF_3. The potassium salt, which was used for most of the studies made, was prepared by adding potassium fluoride to a solution of the trimethyltin salt, when insoluble trimethyltin fluoride was precipitated and evaporation of the resulting solution gave potassium trifluoromethylfluoroborate.

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[1] This work was supported by the U. S. Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

[2] For a preliminary communication see R. D. Chambers, H. C. Clark and C. J. Willis, *Proc. Chem. Soc.*, 114 (1960).

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