

mediates, ClBrO_2 and perhaps OBrOCl , in the two processes. ClBrO_2 may be of analogous structure to that of ClClO_2 investigated by Taube and Dodgen²¹; these authors consider, however, the terminal chlorine as positively charged, although they do not exclude the possibility that their intermediate has the structure OClOCl . It may be suggested therefore that whereas the chloride ions interact with H_2BrO_3^+ at a comparatively fast rate, the formation of BrO_2Cl requires another pre-equilibrium, namely, the dehydration of H_2BrO_3^+ . It should be noted that Y-BrO_2 might undergo a redox reaction by a different mechanism; if Y-BrO_2 is attacked by another Y^- , then $\text{OBrOY} + \text{Y}^-$ may be formed, which will eventually decompose to $\text{OY}^- + \text{BrO}_2^-$. This is consistent with the "third type" reactions formulated by Edwards²² and explains the catalytic effects of halide ions on the halate reduction reactions. This type of catalyzed reduction may occasionally proceed fast enough to consume the YBrO_2 as soon as it is

(21) H. Taube and H. Dodgen, *J. Am. Chem. Soc.*, **71**, 3330 (1949).
 (22) J. O. Edwards, *Chem. Revs.*, **50**, 455 (1952).

formed; in this case the reaction will be first order in Y^- , but no $\text{XO}_3^- - \text{H}_2\text{O}$ oxygen exchange will be induced. Attempts to detect a catalytic effect of bromide ions on the bromate oxygen exchange have failed owing to the fast reduction of bromate; this is an analogous result to that of Hoering⁴ who failed to detect a catalytic effect of chloride in the chlorate-water oxygen exchange. On the other hand some induced $\text{BrO}_3^- - \text{H}_2\text{O}$ exchange was found on reduction of bromate by iodide ions.²³

It may be concluded that the mechanism of oxygen exchange by a bimolecular substitution is not limited to weak acids like hypochlorous and hypobromous acids²⁴ or to those of intermediate strength like nitrous⁶ or iodic acids,⁷ but it may be extended to include the conjugate acids of nitric or bromic acids; furthermore this mechanism includes cases where the formation of an acid anhydride originating from two acid molecules has been postulated, e.g. the formation of nitrogen trioxide in the nitrate water exchange.⁸

(23) M. Anbar and H. Taube, unpublished.

(24) M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **80**, 1073 (1958).

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Invariability of the α -Parameter of Certain Salts with Change in Solvent

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The K_A -values of tetra-*n*-butylammonium perchlorate have been determined in seven one-component solvents ranging in D -value from 9.9 to 25.2. It is found that for five of the solvents, each of which consist of but one molecular species, the most probable relation between $\log K_A$ and $1/D$ is a linear one, thereby showing that the α -parameter of this salt has the same value in each of the solvents. The appreciable deviations from the straight line (so established), found for the solvents ethylene chloride and 1,2-dichloropropane, each of which consist of two molecular species, are shown to conform with the expectation that the effective dielectric constant of each of these solvents in the salt solution should be considerably greater than its macroscopic value. The K_A -values of tetra-*n*-butylammonium picrate, obtained by other investigators in seven one component solvents with D -values ranging from 5.04 to 34.69, are shown to vary linearly with $1/D$, thus warranting the same conclusion regarding the constancy of its α -parameter.

For many years prior to 1955 the most widely used theoretical expression for the relation between the dissociation constant of a salt in any solvent (of sufficiently low dielectric constant), the temperature, the dielectric constant of the solvent and the interionic distance in associated ion pairs (*viz.*, the α -parameter) was that derived by Bjerrum.³ As pointed out by Harned and Owen⁴ "the most noteworthy shortcoming of the Bjerrum model is its inability to follow the variation in the dissociation constant K with the dielectric constant D of the solvent without sometimes requiring highly specific dependence of the α -value upon the solvent." Some examples of this anomalous dependence of the α -parameter of a salt on the solvent are listed in a recent résumé of this subject by Kraus.⁵

It was recognized by those conversant with the Bjerrum theory that it had certain inherent

defects, partly mathematical and partly physical. These defects have been summarized and critically discussed by Fuoss.⁶ That aspect of this theory which is of particular interest in this investigation is the theoretical basis for obtaining the fraction of the pairs of oppositely charged ions which is to be counted as associated ion pairs. According to the Bjerrum theory the number of pairs of ions which are so counted is not restricted solely to those pairs which exist in "physical contact." Two oppositely charged ions are said to be in "physical contact" when the distance between them is sufficiently small to prevent the intervention of solvent molecules. (If, of course, the solvent molecules react to form a stable complex with either of the ions, then these complexing solvent molecules constitute an integral part of that ion.) Fuoss⁶ has given justification for his conclusion that this feature of the Bjerrum theory is untenable. In an earlier article⁷ the advantages of counting

(1) Aeronutronic Systems, Inc., Newport Beach, California.

(2) Postdoctoral Fellow at U.C.L.A., 1961.

(3) N. Bjerrum, *Kgl. Danske Videnskab. Selskab.*, **7**, No. 9 (1926).

(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 294.

(5) C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

(6) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958). See also R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959, pp. 207-223.

(7) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **79**, 3309 (1957).

as associated ion pairs *only* those pairs which are in "physical contact" are presented.

This basis for counting associated ion pairs was proposed by Denison and Ramsey.⁸ From a thermodynamic consideration of a stepwise process for bringing about the change from an associated ion pair (with interionic distance equal to a) to the two free ions (with interionic distance sufficiently greater than a to permit intervention of solvent molecules), an approximate equation was obtained

$$-\ln K = \ln K_A = \epsilon^2/aDkT \quad (1)$$

where K and K_A are the dissociation constant and the association constant, respectively; ϵ , the electronic charge; a , briefly designated the "contact distance" (the a -parameter); D , the dielectric constant of the pure solvent and T , the absolute temperature. According to this equation, the value of the logarithm of K_A of a given salt at a certain temperature should vary linearly with the reciprocal of the dielectric constant of the solvent if its a -parameter has the same value in different solvents, *i.e.* is independent of the dielectric constant of the solvent. The results obtained by Fuoss and Kraus⁹ with tetraisoamylammonium nitrate in a series of dioxane-water mixtures were shown⁸ to conform quite satisfactorily with this requirement.

Equation 1 involves in its derivation the approximation that the value of the free energy of solution of a pair of *uncharged* ions is independent of their distance of separation. If this approximation is not made, it can be readily shown that equation 1 becomes

$$\ln K_A = \ln K_A^0 + \epsilon^2/aDkT \quad (2)$$

where K_A^0 is, according to the thermodynamic derivation, the association constant of the two *uncharged* ions in the solution.

Fuoss⁴ has derived equation 2 by an alternative method thereby obtaining an expression for K_A^0 in terms of the a -parameter. His resulting equation is

$$\ln K_A = \ln(4\pi N a^3/3000) + \epsilon^2/aDkT \quad (3)$$

where N is Avogadro's number. It may be noted that in the derivation of this equation, as in that of equation 2, the predominant force considered to be operative in determining the stability of the associated ion pair is that due to charge-charge interaction. This would be substantially the only force acting to stabilize the associated ion pair if both ions were electrically symmetrical (*i.e.* without an internal dipole moment) and if their mutual polarization at "contact" were entirely negligible.

In a number of recent investigations Fuoss and collaborators¹⁰ have determined the effect of vary-

(8) J. T. Denison and J. B. Ramsey, *J. Am. Chem. Soc.*, **77**, 2615 (1955).

(9) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 1019 (1933).

(10) (a) R. M. Fuoss and C. A. Kraus, *ibid.*, **79**, 3304 (1957). (b) F. Accascina, A. D'Aprano and R. M. Fuoss, *ibid.*, **81**, 1058 (1959). (c) F. Accascina, S. Petrucci and R. M. Fuoss, *ibid.*, **81**, 1301 (1959). (d) R. M. Fuoss and F. Accascina, *Proc. Natl. Acad. Sci., U. S.*, **45**, 1383 (1959). (e) R. M. Fuoss and E. Hirsch, *J. Am. Chem. Soc.*, **82**, 1013 (1960). (f) E. Hirsch and R. M. Fuoss, *ibid.*, **82**, 1018 (1960).

ing the D -value of the solvent on the K_A -value of certain salts (which fall within the purview of equation 3) by use of a series of mixtures of two solvents which, in their pure state, differ appreciably in dielectric constant. They found that for each such salt used the value of $\log K_A$ varied linearly, and quite precisely so, with the reciprocal of the dielectric constant of the solvent mixture. It may be noted that such a linear relation between $\log K_A$ and $1/D$ is not given by the Bjerrum equation. By adoption of some reasonable value of the a -parameter (say 5.0×10^{-8} cm.), it can be shown that the graph obtained by plotting the values of $\log K_A$ (as ordinates), calculated by this equation, for a series of values of D , against $1/D$ (as abscissae) has an appreciable concavity upwards.

At the time ethylidene chloride was first used as a solvent in conductometric work,¹¹ it was found that the value of the association constant of the salt, *o*-chlorophenyltrimethylammonium perchlorate, in this solvent was some ten-fold greater than its value in ethylene chloride. In view of the Bjerrum theory this finding seemed anomalous for two reasons: (1) the difference between the D -values of these two solvents (~ 0.3) was much too small in itself to account for such a large difference in the K_A values and (2) there was no apparent justification for considering the value of the a -parameter of this salt to be appreciably different in these two solvents.

That this seeming peculiarity was not a unique characteristic of this salt was soon confirmed by the results obtained with five other salts.^{8,12} The K_A -value of each of these salts was likewise much (from 8- to 10-fold) greater in ethylidene chloride than its value in ethylene chloride. In the meantime several investigators¹³ had shown that the K_A -values of a number of other salts were also several fold greater in ethylidene chloride than their corresponding values in ethylene chloride.

To account for the very large difference in the K_A -values of a salt in these two solvents, two assumptions were made,^{8,12}

(1) That the a -parameter of any salt had the same value in these two solvents.

(2) That the "effective" (or microscopic) dielectric constant of ethylene chloride, that is, the dielectric constant of this solvent, existing in the near vicinity of an ion, which is effective in determining the stability of an associated ion pair, is appreciably greater than the measured (macroscopic) dielectric constant of pure ethylene chloride.

Adoption of the first of these two assumptions entails the acceptance of the general assumption that the a -parameter of any salt has the same value in all solvents at the same temperature, provided the solvents are restricted to those whose molecules do not interact with either of the ions to form a chemically bonded complex. The plausibility of this assumption has been much enhanced by the numerous results obtained by Fuoss and

(11) J. B. Ramsey and E. L. Colichman, *ibid.*, **69**, 3041 (1947).

(12) J. T. Denison and J. B. Ramsey, *J. Chem. Phys.*, **18**, 770 (1950).

(13) (a) F. Accascina, E. L. Swartz, P. L. Mercier and C. A. Kraus, *Proc. Natl. Acad. Sci., U. S.*, **39**, 917 (1953). (b) F. H. Healey and E. A. Martell, *J. Am. Chem. Soc.*, **73**, 3296 (1951).

collaborators¹⁰ which are quite consistent with it in that the values of $\log K_A$ of each of several salts used were found to vary linearly with the reciprocal of the dielectric constant of the solvent. It is seen that according to equation 2 (or 3) such a linear relation can exist if, and only if, the value of the α -parameter of any salt does not change with change in the solvent.

Reasons for the adoption of the second of these two assumptions have been presented previously.¹² The results of two more recent investigations have provided additional support for it. The first of these pertains to the effect of an externally applied electric field on the dielectric constant of substances in the pure liquid state. In their determination of the effect of the application of strong electric fields (up to 103 kilovolts per centimeter) on the dielectric constant of various liquids, Piekara, *et al.*,¹⁴ have found that the dielectric constant of ethylene chloride increases with increase in the intensity of the applied electric field (which is opposite to the effect of an applied field on the dielectric constant of other polar liquids whose molecules are known to exist in but one form). This so-called "negative saturation effect," shown by ethylene chloride, is attributed to the influence of the applied field on the equilibrium between the *gauche* (polar) and *trans* (non-polar) molecules of ethylene chloride, which results in an increase in the ratio of *gauche* to *trans* molecules and therefore an increase in the dielectric constant. The electric field of an ion would be expected to have the same effect on this ratio as does the externally applied field and thereby cause the dielectric constant of the ethylene chloride which is near enough to an ion to be influenced by its field to be appreciably greater than that of pure ethylene chloride.

A comparison of the infrared absorption spectra of ethylene chloride in the presence of the dissolved salt, tetra-*n*-butylammonium perchlorate, with that in the pure state¹⁵ has provided a second and more direct substantiation of the second assumption. The results show that the ratio of *gauche* to *trans* molecules has a considerably larger value in the salt solutions ($\sim 30\%$ greater in 0.77 v.f. and $\sim 45\%$ greater in 1.23 v.f. solution) than its value, 1.3, in pure ethylene chloride; the value found by Mizushima, *et al.*¹⁶

Evidence in support of the assumption that the α -parameter of a given salt has the same value in different one-component solvents has not as yet been adduced. Equation 2 provides a means for testing this assumption. Results of this investigation, along with those of other investigators, are presented which give substantial evidence for its validity. In addition it is shown, more convincingly than previously, that the effective dielectric constants of the two solvents, ethylene chloride and 1,2-dichloropropane, each of which consists of two molecular species, are appreciably

greater than their respective macroscopic dielectric constants.

Experimental

The seven solvents used were ethylidene chloride, $\text{CH}_2\text{ClCH}_2\text{Cl}$; ethylene chloride, $\text{CH}_2\text{ClCH}_2\text{Cl}$; 2,2-dichloropropane, $\text{CH}_3\text{CCl}_2\text{CH}_3$; 1,2-dichloropropane, $\text{CH}_2\text{ClCHClCH}_3$; *o*-dichlorobenzene, $\text{C}_6\text{H}_4\text{Cl}_2$; 2-butanone, $\text{CH}_3\text{COC}_2\text{H}_5$; benzonitrile, $\text{C}_6\text{H}_5\text{CN}$. The D -values of these solvents cover the range from 9.9 to 25.2 at 25°. The salt, tetra-*n*-butylammonium perchlorate, $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$, had the desired characteristics in that both of its ions are electrically symmetrical and its solubility in each of the seven solvents is sufficient to permit conductance measurements over the concentration range of interest.

This salt was prepared by metathesis of recrystallized tetra-*n*-butylammonium iodide (Eastman white-label grade) with a slight excess of silver perchlorate (which had been recrystallized from 60% perchloric acid) in 95% ethanol. The filtrate from the silver iodide was evaporated until crystals appeared, then cooled slowly and filtered. The crystals so obtained were washed repeatedly with cooled water until the filtrate gave a negative test for silver ion (as shown by addition of an acidified KI solution). This product was twice recrystallized from warm ($\sim 80^\circ$) ethyl acetate, to which, after cooling, a small quantity of pentane was added. After drying for 36 hr. *in vacuo* in an Abderhalden drying apparatus, the salt had an uncorrected melting point of 213.3°, in satisfactory agreement with the value, 213°, reported by Reynolds and Kraus.¹⁷

Treatment of Solvents.—All the solvents, excepting 2,2-dichloropropane, were Eastman white label products. The procedure used to prepare 2,2-dichloropropane was that described by Friedel and Silva.¹⁸ This consisted of controlled chlorination of isopropyl chloride (Eastman white label grade) at a temperature kept below 15° and under continuous illumination by a 200-watt incandescent electric light one inch from the reaction flask. The product, from which hydrogen chloride had been removed with aqueous sodium carbonate, was washed twice with saturated sodium chloride solution and finally dried over anhydrous sodium sulfate for 12 hr.

The 2,2-dichloropropane so obtained and each of the other six solvents were fractionally distilled through a three foot vacuum jacketed column filled with glass helices. With the exception of 2-butanone (methyl ethyl ketone) and benzonitrile, this distillation was carried out in the presence of calcium hydride. The 2-butanone was refluxed for about 3 hr. in the presence of a mixture of the solids, calcium oxide and potassium permanganate, prior to distillation, a procedure found satisfactory by Sachs and Fuoss.¹⁹ Boiling stones alone were present during the reduced pressure distillation of benzonitrile. All but a very small portion of each of the solvents was obtained as distillate either at constant temperature or within a very small temperature range. The usual precautions were taken to avoid contact with moisture in the air during distillation, in storage, and in transference of the solvent to the conductance cell. The added precaution of storing over activated silica gel was taken (and found necessary) with ethylidene chloride.

The boiling points (at barometric pressure unless otherwise specified) and the maximum specific conductances, L_{max} , at 25° of the solvents were (1) ethylene chloride, 83.2–83.3°, with L_{max} of 8×10^{-10} ohm⁻¹ cm.⁻¹; (2) ethylidene chloride, 57.0–57.1°, with L_{max} of 3×10^{-9} ; (3) 1,2-dichloropropane, 95.9–96.2°, with L_{max} of 6×10^{-10} ; (4) 2,2-dichloropropane, 69.0–69.7°, with L_{max} of 4×10^{-9} ; (5) *o*-dichlorobenzene, 81.0–82.0° at 30.9 to 32 mm. pressure, with L_{max} of 6×10^{-10} ; (6) 2-butanone, 79.5° with L_{max} of 1.8×10^{-8} ; (7) benzonitrile, 84° at 22 mm. with L_{max} of 1.1×10^{-8} . Since the *o*-dichlorobenzene used (Eastman white label) is listed as 99 + % pure and since *p*-dichlorobenzene is the most likely organic impurity present, a gas chromatogram of this distilled product along with that of a known mixture of this product and *p*-dichlorobenzene (Eastman white label grade) were obtained. From these it was found that the distilled product contained somewhat less than 0.5

(17) M. B. Reynolds and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 1709 (1948).

(18) C. Friedel and R. D. Silva, *Compt. rend.*, **73**, 1379 (1871).

(19) F. M. Sachs and R. M. Fuoss, *J. Am. Chem. Soc.*, **75**, 5172 (1953).

(14) (a) A. Piekara and A. Chelkowski, *J. Chem. Phys.*, **25**, 794 (1956). (b) A. Piekara, S. Kieflich and A. Chelkowski, *Arch. sci. (Geneva)*, **12**, Fasc. spec., 5965 (1959), (in English).

(15) Y. Harry Inami and J. B. Ramsey, *J. Chem. Phys.*, **31**, 1297 (1959).

(16) (a) Y. Morino, I. Watanabe and S. Mizushima, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **39**, 396 (1942). (b) I. Watanabe, S. Mizushima and Y. Morino, *ibid.*, **39**, 301 (1942).

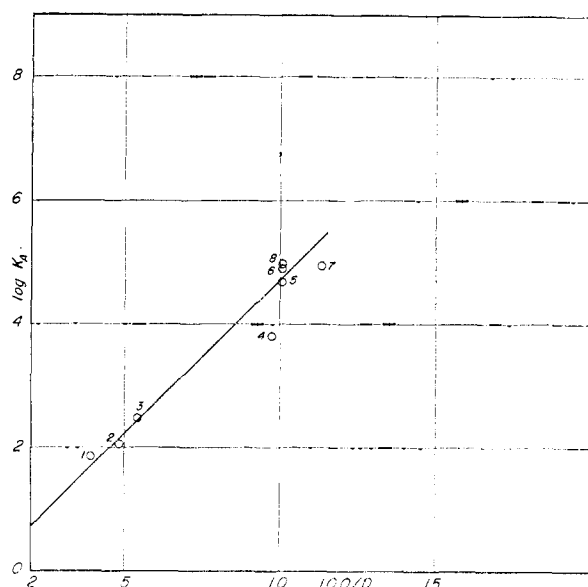


Fig. 1.—Dependence of the association constant of $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ on the macroscopic dielectric constant of the solvent. Point numbers correspond to those given to the solvents in Table II.

mole per cent. of *p*-dichlorobenzene as the only foreign organic substance present.

In Table I are given the values at 25° which have been accepted for the density d , the dielectric constant D , and the viscosity η , of each of the solvents along with references to their origins.

TABLE I

PROPERTIES OF SOLVENTS AT 25°

| | d , g./ml. | D | η , poise |
|---------------------------|----------------------|--------------------|-----------------------|
| Ethylidene chloride | 1.168 ⁸ | 9.90 ⁸ | 0.00455 ⁸ |
| Ethylene chloride | 1.241 ⁸ | 10.23 ⁸ | .00778 ⁸ |
| 1,2-Dichloropropane | 1.153 ²⁰ | 8.78 ²⁰ | .00795 ²⁰ |
| 2,2-Dichloropropane | 1.085 ²¹ | 9.91 ²² | .00663 ²³ |
| <i>o</i> -Dichlorobenzene | 1.300 ^{18a} | 9.93 ²⁴ | .01271 ^{18a} |
| 2-Butanone | 0.7998 ²³ | 18.4 ¹⁹ | .00377 ¹⁹ |
| Benzonitrile | 1.0007 ²³ | 25.2 ²⁴ | .01224 ²³ |

Conductance Measurements.—The sensitivity of the alternating current bridge, used previously,⁸ was considerably improved (1) by providing more adequate shielding which included all leads as well as the conductance cell in the thermostat, and (2) by replacing the 60 cycle rejection filter with a parallel passive resonance filter, tuned to 2500 cycles/second, which was inserted between the amplifier and the oscilloscope.

Two conductance cells of the Erlenmeyer type⁹ were used having cell constants equal to 0.1543 and 0.1473 which were determined in the way previously described.⁸

Preparation of Solutions.—The procedure followed in preparing the original solution and in making successive dilutions has been described.⁸

(20) K. A. Stern and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 1983 (1955).

(21) E. H. Huntress, "The Preparation, Properties, Chemical Behavior and Identification of Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 990.

(22) A. Turkevich and C. P. Smyth, *J. Am. Chem. Soc.*, **62**, 2468 (1940).

(23) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950, p. 257.

(24) A. A. Maryott and E. R. Smith, Natl. Bur. Standards Circular No. 514 (1951).

Results

The value of the association constant, K_A , and the limiting equivalent conductance, Λ_0 , of tetra-*n*-butylammonium perchlorate in each of the seven solvents was obtained by use of the equation developed by Shedlovsky,²⁵ namely, in the way

$$1/\Delta S(z) = [c\Delta f^2 S(z)]K_A/\Lambda_0^2 + 1/\Lambda_0$$

previously described.⁸ To establish the most probable straight line relation between $1/\Delta S(z)$ and $c\Delta f^2 S(z)$, the conductances at not less than five concentrations of the perchlorate (covering the range from $\sim 10^{-4}$ to $\sim 10^{-5}$ volume formal) were determined. In each solvent two independent determinations of the value of K_A were carried out. In most cases the two values of K_A agreed within less than 2%; in no case did they differ by more than 4%. The two values of Λ_0 differed by less than 1% in all cases.

In Table II are given the average of the two independently determined values of K_A and Λ_0 in each of the seven solvents. Included are the values of these constants found by Reynolds and Kraus¹⁷ for this salt in acetone.

TABLE II

CONSTANTS OF $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ IN VARIOUS SOLVENTS AT 25°

| Solvent | Λ_0 | $K_A \times 10^{-3}$ | $\log K_A$ | $100/D_{\text{macro}}$ |
|--|-------------|----------------------|------------|------------------------|
| (1) $\text{C}_6\text{H}_5\text{CN}$ | 46.02 | 0.0753 | 1.877 | 3.97 |
| (2) CH_2COCH_3 | 182.5 | .114 | 2.057 | 4.88 |
| (3) $\text{CH}_2\text{COC}_2\text{H}_5$ | 143.5 | .302 | 2.480 | 5.43 |
| (4) $\text{CH}_2\text{ClCH}_2\text{Cl}$ | 65.2 | 6.41 | 3.807 | 9.77 |
| (5) CH_2CHCl_2 | 109.7 | 46.7 | 4.669 | 10.10 |
| (6) $\text{CH}_2\text{CCl}_2\text{CH}_2$ | 84.3 | 80.6 | 4.906 | 10.08 |
| (7) $\text{CH}_2\text{ClCHClCH}_3$ | 56.5 | 91.6 | 4.962 | 11.36 |
| (8) <i>o</i> - $\text{C}_6\text{H}_4\text{Cl}_2$ | 42.3 | 93.4 | 4.970 | 10.07 |

The values of Λ_0 and K_A in ethylene chloride are in excellent agreement with those found by Gleysteen and Kraus,²⁶ namely, 65.4 and 6.49×10^3 , respectively. It may be noted that the association constant of this salt has (like numerous others referred to above) a very much greater value in ethylidene chloride than it has in ethylene chloride.

A plot of the values of $\log K_A$ against the values of $100/D_{\text{macro}}$ is shown in Fig. 1. The results plotted in Fig. 1 provide justification for the conclusion that, for the six monomolecular solvents (numbers 1, 2, 3, 5, 6 and 8), the most probable relation between $\log K_A$ and $100/D$ is a linear one. The best linear relation between these six points (established by the method of least squares) is given by the straight line.

The large deviations from this straight line shown by the points (numbered 4 and 7) for ethylene chloride and 1,2-dichloropropane accord with our previous conclusion regarding the effective dielectric constants of such solvents, namely, that their D_{eff} -values should be considerably greater than their D_{macro} -values.

(25) T. Shedlovsky, *J. Frank. Inst.*, **220**, 739 (1938).

(26) L. F. Gleysteen and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 451 (1947).

It is seen that according to equation 2 [applicable to $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$] a linear relation between $\log K_A$ and $100/D$ should result provided the α -parameter of salt has the same value in each of the solvents. From the slope (0.502) of the straight line (in Fig. 1) the value of the α -parameter of $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ in each of the six solvents (each of which consist of but one molecular species) is determined ($\alpha = \epsilon^2/230.3 kT \cdot \text{slope}$) and found to be 4.85×10^{-8} cm.

From the fact that the single molecular species of which each of these six solvents is composed differ considerably from each other in their structure, it follows that the value of the α -parameter of this perchlorate is independent of the structure of the molecules of the solvent in which it is dissolved. On this basis the assumption that the α -parameter of this perchlorate will have this same value (*viz.*, 4.85×10^{-8} cm.) in the two solvents (each of which consists of two molecular species), $\text{CH}_2\text{ClCH}_2\text{Cl}$ and $\text{CH}_2\text{ClCHClCH}_3$, is considered to be warranted. Thus the assumption (*ad hoc* when made^{8,12}) that the α -parameters of the six different perchlorates then used have the same respective values in ethylene chloride as they have in ethylidene chloride is substantiated.

The effective dielectric constant, D_{eff} , of each of the two bimolecular solvents will, therefore, be that value which is consistent with an α -parameter equal to 4.85×10^{-8} cm. This value could be estimated from visual inspection of Fig. 1. It is preferable to calculate its value by use of the equation of the straight line drawn in Fig. 1. The slope of this line (calculated by the method of least squares) is 0.502, and its intercept on the $\log K_A$ axis (at $100/D = 0$) is -0.245 . It follows from equation 2 that the equation of this straight line is

$$\log K_A = -0.245 + 0.502 (100/D_{\text{eff}})$$

Substitution of the respective values found for $\log K_A$ (1) in ethylene chloride, *viz.*, 3.81, and (2) in 1,2-dichloropropane, *viz.*, 4.97, gives the D_{eff} of the former solvent the value 12.4 ($D_{\text{macro}} = 10.23$) and of the latter, 9.64 ($D_{\text{macro}} = 8.78$).

Discussion

As previously noted, equation 2 is restricted in its application to salts with both ions electrically symmetrical. In such salts the force acting to stabilize the associated ion pair is considered to be that due primarily to charge-charge interaction. If either of the ions of a salt is electrically asymmetrical, then in addition to the stabilizing force due to charge-charge interaction, there will exist the force produced by charge-dipole interaction. Picrates of electrically symmetrical cations, much used in conductimetric investigations, are examples of salts in which there exists this additional force due to charge-dipole interaction. Accascina, D'Aprano and Fuoss^{10b} have pointed out that for such salts equation 2 should be replaced by

$$\ln K_A = \ln K_A^0 + \epsilon^2/aDkT + \mu\epsilon^2/DkTd^3 \quad (4)$$

where μ is the dipole moment of the electrically asymmetrical anion and d is the distance from the

center of the cation to the center of the dipole of the anion when the cation and anion exist in an associated ion pair. These investigators^{10b} used a series of mixtures of methyl alcohol and water to obtain solvents with different D -values. With three mixtures ranging in D -value from 32.66 to 37.53, they found that the value of $\log K_A$ of tetraethylammonium picrate varied linearly with $1/D$.

In view of our results with $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ in a series of one component solvents and these findings of Fuoss, *et al.*,¹⁰ it seemed very probable that a linear relation should be found to exist between the values of $\log K_A$ of a salt such as a tetraalkylammonium picrate, and the reciprocal of the dielectric constants of several *one component* solvents.

The salt, tetra-*n*-butylammonium picrate, has been more frequently used and in a greater variety of solvents than has any other salt. In Table III are given the values of K_A reported for this salt in seven different solvents along with the values of D_{macro} used in the respective investigations.

TABLE III

CONSTANTS OF $(n\text{-C}_4\text{H}_9)_4\text{NPi}$ IN VARIOUS SOLVENTS AT 25°

| Solvent | $K_A \times 10^{-3}$ | $\log K_A$ | D | $100/D$ |
|---|----------------------|------------|-------|---------|
| (1) $\text{C}_6\text{H}_5\text{NO}_2^a$ | 0.0074 | 0.87 | 34.69 | 2.88 |
| (2) $\text{CH}_3\text{COCH}_3^b$ | 0.0488 | 1.65 | 20.47 | 4.88 |
| (3) $\text{C}_6\text{H}_5\text{N}^c$ | 2.44 | 3.39 | 12.01 | 8.33 |
| (4) $\text{CH}_2\text{ClCH}_2\text{Cl}^d$ | 4.39 | 3.64 | 10.23 | 9.77 |
| (5) $\text{CH}_2\text{CHCl}_2^e$ | 22.0 | 4.34 | 10.00 | 10.00 |
| (6) $\text{C}_6\text{H}_5\text{Cl}^f$ | 53200 | 7.73 | 5.63 | 17.8 |
| (7) $m\text{-C}_6\text{H}_4\text{Cl}_2^g$ | 395000 | 8.60 | 5.04 | 19.8 |

^a E. Hirsch and R. M. Fuoss, *J. Am. Chem. Soc.*, **82**, 1018 (1960). ^b M. B. Reynolds and C. A. Kraus, *ibid.*, **70**, 1709 (1948). ^c W. F. Luder and C. A. Kraus, *ibid.*, **69**, 2481 (1947). ^d D. J. Mead, R. M. Fuoss and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936). ^e F. H. Healey and A. E. Martell, *J. Am. Chem. Soc.*, **73**, 3296 (1951). ^f R. L. McIntosh and R. M. Fuoss, *ibid.*, **62**, 506 (1940). ^g F. H. Flaherty and K. H. Stern, *ibid.*, **80**, 1034 (1958).

A plot of these values of $\log K_A$ against $100/D_{\text{macro}}$ is shown in Fig. 2.

It is apparent that the most probable relation between the points corresponding to the six solvents (numbers 1, 2, 3, 5, 6 and 7) which consists of but one molecular species is a linear one. It is seen that the point (number 4) for ethylene chloride deviates appreciably from the best straight line described by these six points and in the direction expected. The effective dielectric constant D_{eff} of ethylene chloride in the presence of the picrate may be determined (as was done in the presence of the perchlorate) from the slope, 0.460, and the intercept, -0.470 , on the $\log K_A$ axis (at $100/D = 0$) of this best straight line. Reformulation of equation 4 gives

$$\log K_A = \text{slope} (100/D_{\text{eff}}) + \text{Intercept}$$

which becomes in this case

$$3.64 = 0.460 (100/D_{\text{eff}}) - 0.470$$

Solution of this equation gives 11.2 for the value of D_{eff} of ethylene chloride in the presence of the picrate.

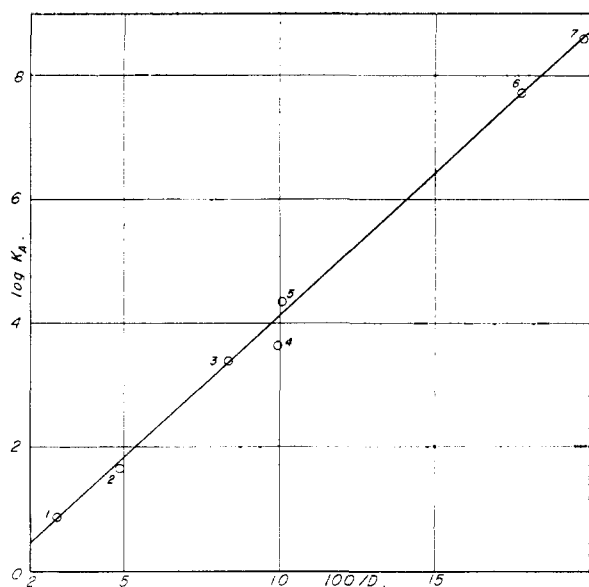


Fig. 2.—Dependence of the association constant of $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{Pi}^-$ on the macroscopic dielectric constant of the solvent. Point numbers correspond to those given to the solvent in Table III.

It may be significant that the enhancement of the dielectric constant of ethylene chloride in the

presence of the picrate (from 10.23 to 11.2) is less than that in the presence of the perchlorate (from 10.23 to 12.4). Results available at present are insufficient to warrant a conclusion regarding the dependence of the magnitude of this enhancement on the properties of the ions of the dissolved salt. In view of our interpretation of this enhancement it seems reasonable to predict that it (this enhancement) will be found to increase (1), with decrease in the size of ions of like charge and (2), with increase in the charge of ions of the same size.

The slope of the straight line in Fig. 2 is not alone sufficient in this case to permit evaluation of the a -parameter of this picrate. As seen from equation 4 the slope is

$$d \log K_A/d(100/D) = (0.4343/100)(\epsilon^2/akT + \mu\epsilon/d^2kT)$$

The linearity between $\log K_A$ and $100/D$ does, however, warrant the conclusion that the a -parameter of this picrate has the same value in each of the seven solvents. If this were not so, the change in the value of ϵ^2/akT (with change in D) would need to be equal and opposite in sign to that of $\mu\epsilon/d^2kT$; a restriction which seems extremely unlikely. It seems far more reasonable to presume that the value of μ , the dipole moment of the picrate ion and of the d -parameter of this picrate are constant, independent of the dielectric constant of the solvent

[CONTRIBUTION FROM U. S. BORAX RESEARCH CORPORATION, ANAHEIM, CALIFORNIA]

The Preparation of Boron Monoxide and its Conversion to Diboron Tetrachloride¹

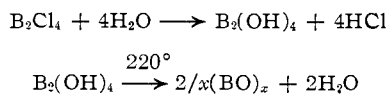
BY A. L. McCLOSKEY, R. J. BROTHERTON AND J. L. BOONE

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Tetrahydroxydiboron was prepared by hydrolysis of tetra-(dimethylamino)-diboron in aqueous hydrochloric acid solution and by neutral hydrolysis of tetraisopropoxy or tetraethoxydiboron. The anomalous hydrolysis of tetramethoxydiboron is also discussed. Boron monoxide was prepared by dehydration of tetrahydroxydiboron and its possible structure discussed. Boron monoxide was converted to diboron tetrachloride by reaction with boron trichloride at approximately 200°. This conversion completes a series of reactions which establishes the integrity of the boron-boron bond in a number of related compounds.

Introduction

Wartik and Apple prepared tetrahydroxydiboron, $\text{B}_2(\text{OH})_4$, by the hydrolysis of diboron tetrachloride and converted it into boron monoxide, $(\text{BO})_x$, by dehydration at 220°. The boron mon-



oxide prepared by this procedure was white, or colorless, and was stable in vacuum up to about 500°. However, at 650° it was converted to an amber form which was assumed to be the same as

(1) The research reported in this document was supported by Wright Air Development Division, Air Research and Development Command, United States Air Force, under contract AF 33(616)-5931. A portion of this research was reported in a preliminary communication, A. L. McCloskey, J. L. Boone and R. J. Brotherton, *J. Am. Chem. Soc.*, **83**, 1766 (1961).

(2) T. Wartik and E. F. Apple, *ibid.*, **77**, 6400 (1955).

the boron monoxide reported from the reaction of zirconium oxide with elemental boron at elevated temperature.³ More recently boron monoxide was reported as a product of the reaction of boric oxide with elemental boron, and presumably this is also a high-temperature form.⁴ However, a number of inconsistencies exist concerning the nature of the so-called low-temperature and high-temperature modifications and the relation between these forms is not well understood.

Work has now been performed which gives a better insight into the boron monoxide prepared directly from compounds known to contain boron-boron bonds. Since very little information was available concerning this substance, it was essential that a comparison be made between previously reported boron monoxide and that available

(3) E. Zintl, W. Morawietz and E. Gastinger, *Z. anorg. u. allgem. Chem.*, **245**, 8 (1940).

(4) F. A. Kanda, A. J. King, V. A. Russell and W. Katz, *J. Am. Chem. Soc.*, **78**, 1509 (1956).