NOTES

Molar Heats of Solution of *n*-Butylboric Acid and Tri-*n*-butylboric Oxide[1]

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Received April 14, 1954

n-Butylboric acid (*n*-butane boronic acid) and its anhydride, tri-*n*-butylboric oxide, form an interesting pair of compounds. At room temperature the acid is a solid, while the oxide is a liquid. One is confronted with the unusual circumstance of having a liquid anhydride which reacts with water to produce the solid acid. In our program of study of the thermochemistry of boron compounds we determined the heats of solution of both *n*-butylboric acid and tri-*n*-butylboric oxide with the intention of also determining their heats of formation. Since it appears that this latter objective will be postponed indefinitely we are reporting the heat of solution data at this time.

Experimental.—A description of the heat of solution calorimeter and details of its operation and calibration have been given by us in a previous publication.[3] As before the calorimeter contained 520.0 (±0.1) g. of water in all experiments and its heat capacity when filled was 568.4 ± 1.2 cal./deg.

n-Butylboric acid and tri-*n*-butylboric oxide were prepared and kindly supplied to us by Dr. Charles Ericson of this Laboratory who used the method of Mattraw.[4] Analyses showed the samples to be pure, though the difficulty of boron analysis with this type of compound results in precision no greater than about 1%. Impurities which might have been present in quite small amounts would have had structure and properties similar to the compounds under study.

Results and Discussion.—Tri-*n*-butylboric oxide hydrolyzes to yield *n*-butylboric acid according to the equation

$$(C_4H_9BO)_3 + 3H_2O + Aq = 3C_4H_9B(OH)_2\cdot Aq \quad (1)$$

A series of five determinations of the heat of this hydrolysis yielded an average of $\Delta H = -11.6 \pm 0.15$ kcal./mole of $(C_4H_9BO_3)_3$ when the average concentration of the *n*-butylboric acid produced was 0.024 *m*. The actual range of concentration varied from about 0.05 to 0.007 *m* and although there was a hint of slight decrease of heat of hydrolysis with increasing concentration, such dependence, if it exists in the concentration range studied, lies within the accuracy of the measurements. Difficulties were introduced in these measurements by the low solubility and slow rate of dissolution of *n*-butylboric acid which tended to stick to stirrer and sample tubes when produced in the calorimeter according to reaction 1.

Five measurements of the heat of solution of small samples of *n*-butylboric acid yielded an average heat of solution of $\Delta H = 2.67 \pm 0.06$ kcal./mole when the average concentration of the acid was 0.008 *m*, with the actual concentrations ranging between 0.006 and 0.009 *m*. No trend was observed in the results. The accuracy of the measurements was low (±2.3%) because of use of quite small samples necessitated by a very limited supply of the compound.

From the experimental data, assuming no concentration dependence, one calculates that the heat of conversion of the liquid oxide to crystalline acid is exothermic 19.6 kcal./mole of oxide (per 3 moles of acid).

The results may be summarized by the following equations

$$(1)\quad (C_4H_9BO)_3(l) + 3H_2O + Aq \longrightarrow 3C_4H_9B(OH)_2\cdot Aq \quad \Delta H = -11.6 \pm 0.2$$

$$(2)\quad C_4H_9B(OH)_2(c) + Aq \longrightarrow C_4H_9B(OH)_2\cdot Aq \quad \Delta H = 2.7 \pm 0.1$$

$$(3)\quad (C_4H_9BO)_3(l) + 3H_2O \longrightarrow 3C_4H_9B(OH)_2(c) \quad \Delta H = -19.6 \pm 0.4$$

Acknowledgment.—Our thanks are due Dr. Charles Ericson for preparation of the samples. One of us (E.R.V.) wishes to express his appreciation to the Faculty Research Grants Committee and the Office of the Vice President for Research of Cornell University for a grant to purchase a precision platinum resistance thermometer calibrated by the National Bureau of Standards.

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[1] In part from the M.S. thesis of A. S. Dworkin, Cornell University, September, 1951.

[2] Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[3] E. R. Van Artsdalen and A. S. Dworkin, This Journal, **74**, 3401 (1952).

[4] H. C. Mattraw, Thesis, Cornell University, 1950.

Electric Moments from Extrapolated Mixed Solvent Data

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Received April 10, 1954

Many compounds have insufficient solubility in non-polar, non-donor type solvents (such as benzene) to permit determinations of electric moments by the dilute solution method. In many such cases moments have been determined in 1,4-dioxane solution, but the values obtained are generally too high due to solute–solvent hydrogen bonding effects.

Preliminary results of a method intended for the determination of benzene solution moments for compounds not soluble in benzene, through extrapolation to pure benzene of mixed solvent data, are reported here.

A benzene-soluble compound of intermediate moment and exhibiting considerable solvent effect in dioxane solution (*p*-chloroaniline: μ 2.99 benz.; 3.36 diox.)[1] was chosen for the first investigation.

Dielectric constant data were determined as indicated in Fig. 1.

The lines show the variation of dielectric constant of equimolar solutions as a function of mixed solvent environment. The zero molarity line is for pure mixed solvent.

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[1] C. Curran and G. K. Estok, This Journal, **72**, 4575 (1950).

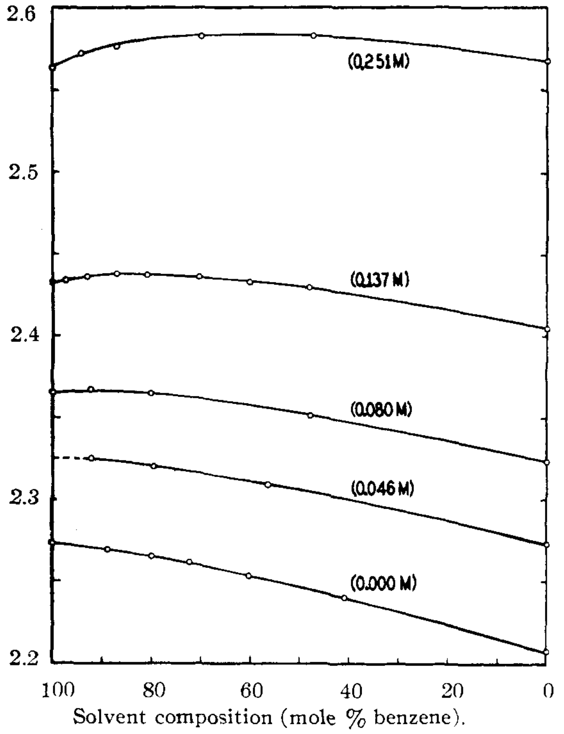

Fig. 1.—Dielectric constant curves for equimolar solutions of *p*-chloroaniline in mixed benzene–dioxane solvent.

Data derived from the 0.251 *M* line did not fit in well, due to excessive concentration, and were not used.

All solutions were weighed so that concentrations could also be expressed in terms of weight fraction solute, w_2. Plots of w_2 *vs.* solvent composition were made for each solute line. Densities were determined for several solutions on the 0.137 *M* line, as well as at several solvent compositions, to permit a plot from which $\Delta d/w_2$ values were obtained.

Data were abstracted from the various plots to permit calculation of electric moments in the following solvent environments: 100% dioxane, 80-20, 60-40, 40-60 and 20-80. The following illustrated the general procedure. For solutions in dioxane values of $\Delta\epsilon$ were taken from each equimolar line to the solvent line. Each such value was divided by w_2 to yield $\Delta d\epsilon/w_2$. These were then extrapolated to $M = 0$ to yield $\Delta\epsilon/w_{2\infty}$. From the density graph $\Delta d/w_2$ was obtained which was sufficiently accurate to be used as $\Delta/w_{2\infty}$. From these data the moment in dioxane solution was calculated.

In a completely similar manner moments were calculated for the other solvent compositions. The moments are plotted in Fig. 2.

Extrapolation to 100 mole % benzene yielded a moment of 2.98 in agreement with a value previously determined in benzene solution.[1]

Several alternate methods of handling the data were tried with essentially equivalent results. Individual moments might also have been determined in several mixed solvent environments without requiring equimolar conditions; however, the method used was more flexible and informative.

Two solute lines (but no solvent line) were run for *p*-nitroaniline, a compound only slightly soluble in benzene. A value of 31.7 for $\Delta\epsilon/w_2$ between the two lines was in agreement with a value of 31.7 between benzene solutions of approximately equal concentration reported earlier.[1]

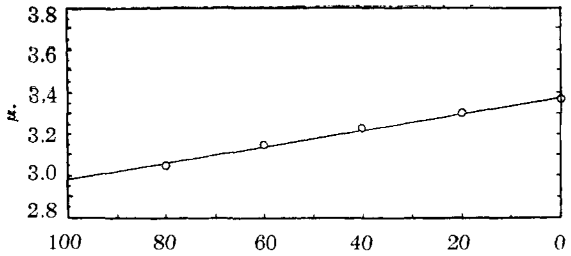

Fig. 2.—Electric moments of *p*-chloroaniline as a function of mixed solvent environment.

Some data by Few and Smith[2] for aniline in mixed benzene–dioxane solvent, determined in connection with an association study, were converted for analysis by one of the alternate extrapolation methods. A value of 2.93 for $\Delta\epsilon/w_{2\infty}$ was obtained in agreement with 2.93 based on other work in benzene solution by the same authors.[3]

Moments by extrapolation should be of value in connection with the following points: (1) benzene solution moments may be had for many compounds not soluble in benzene; (2) solutes which associate in benzene solution (carboxylic acids, amides, etc.) may possibly yield reliable moments by extrapolation; (3) mixed solvents of benzene and a polar solvent (such as morpholine) may prove of value.

Experimental data on *p*-chloro- and *p*-nitroaniline, and other compounds currently being studied will be reported in a later paper.

(2) A. V. Few and J. W. Smith, *J. Chem. Soc.*, 2781 (1949).

(3) A. V. Few and J. W. Smith, *ibid.*, 753 (1949).

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The Dielectric Constant of Liquid Trifluoroacetic Acid[1]

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RECEIVED MAY 17, 1954

There are two widely different sets of data for the dielectric constant of liquid trifluoroacetic acid in the literature: those of Simons and Lorentzen,[3] who report large values and an abnormal positive temperature coefficient, and those of Dannhauser and Cole,[4] who report lower values and a negative temperature coefficient. Prior to the appearance of the more recent publication, we had conducted measurements on this material as part of a program to study the effects of hydrogen bonding on the dielectric properties of various substances. Since special precautions were taken to avoid contamination of this corrosive material, and the dielectric

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(1) Presented before the Division of Physical and Inorganic Chemistry, 125th meeting, American Chemical Society, March, 1954.

(2) Predoctoral Fellow, National Science Foundation, 1952-1953.

(3) J. H. Simons and K. E. Lorentzen, THIS JOURNAL, **72**, 1426 (1950).

(4) W. Dannhauser and R. H. Cole, Jr., *ibid.*, **74**, 6105 (1952).