VOH^{+2} has been called upon in other kinetic studies involving vanadium(III). Ramsey, Sugimoto and DeVorkin[17] have found that rate measurements indicate the VOH^{+2} ion is the predominantly reactive species when vanadium(III) reacts with such "non-oxide"-containing oxidants as iodine, copper(II) and oxygen.

Acknowledgment.—The authors wish to thank Professor J. B. Ramsey for helpful discussions.

LOS ANGELES 24, CALIFORNIA RECEIVED OCTOBER 26, 1951

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[17] J. B. Ramsey, R. Sugimoto and H. DeVorkin, THIS JOURNAL, **63**, 3480 (1941).

[CONTRIBUTION FROM THE SCHOOL OF MEDICINE AND DENTISTRY, UNIVERSITY OF ROCHESTER]

Some Ion-Exchange Studies of the Polymerization of Beryllium[1]

BY ISAAC FELDMAN AND JEAN R. HAVILL

The ion-exchange between beryllium solutions and the ammonium form of Dowex 50 resin was studied to determine the experimental conditions under which polymerization of beryllium begins. At an ionic strength of 0.1, *p*H 4.5, and 37°, the polymerization of beryllium in perchlorate solution begins when its concentration is raised to about 10^{-5} *M*. Increasing the ionic strength to 0.4 appears to increase the extent of polymerization. At *p*H 5.5 beryllium could not be kept completely in solution, even in tracer concentration, without the addition of complexing agents.

In our application of the ion-exchange technique of Schubert[2] to the study of the beryllium–citrate complex,[3] it became necessary to gain more knowledge than was available previously concerning the polymerization of the beryllium ion as a function of *p*H and beryllium concentration.

It has been shown[4] that in macro concentration (above 0.005 *M*) the beryllium ion is readily hydrolyzed and that the initial hydrolysis product polymerizes immediately.

A literature survey has revealed no data pertinent to the subject for solutions containing less than 0.005 *M* beryllium. An extrapolation of the hydrolysis data given in Table I would seem to indicate that at *p*H 4.6[5] and at an ionic strength of 0.1 beryllium is in an unhydrolyzed state when its concentration is less than *ca.* 10^{-4} *M*. However, Schubert and Conn,[6] have pointed out that hydrolyzable elements may form radio-colloids even at *p*H's and concentrations so low that one would infer from macro-measurements that no hydrolysis occurs. We have utilized their suggestion that ion-exchange resins may be used to detect the occurrence of polymerization of ions in low concentrations.

TABLE I

EFFECT OF BERYLLIUM CONCENTRATION ON HYDROLYSIS OF BERYLLIUM AT *p*H4.6; IONIC STRENGTH, *ca.* 0.11; 31°

(See experimental section for details)

Solution titrated	Titrating agent	NaOH added, ml.	% Be hydrolyzed, (approx.)
0.0562 *M* $BeSO_4$	0.0755 *M* NaOH	15.30	83
.0112 *M* $BeSO_4$ in 0.08 *M* $NaClO_4$	.0755 *M* NaOH	2.51	68
.00337 *M* $BeSO_4$ in 0.10 *M* $NaClO_4$	.00653 *M* NaOH in 0.10 *M* $NaClO_4$	5.40	42
.000337 *M* $BeSO_4$ in 0.10 *M* $NaClO_4$	....	0	<7[a]

[a] The *p*H of 3.37×10^{-4} *M* $BeSO_4$ in 0.1 *M* $NaClO_4$ was 4.73, indicating about 7% hydrolysis of beryllium.

Experimental

Materials.—All chemicals other than the beryllium solutions were J. T. Baker C.P. analyzed grade.

The molar concentration of the beryllium isotope, Be^7, was calculated[7] from the radioactivity in mc./ml., as stated by the supplier, the Oak Ridge National Laboratory.

The beryllium perchlorate stock solution was prepared by dissolving beryllium metal (spectroscopically better than 99.9% pure) in a slight excess of perchloric acid, filtering the insoluble residue, and diluting to the desired volume. The concentration of this stock solution was determined by the alkannin method.[8] The beryllium sulfate stock solution was prepared from $BeSO_4 \cdot 4H_2O$, which had been recrystallized four times from water, and was standardized by ignition of an aliquot to beryllium oxide.

The Dowex 50 resin received from the manufacturer was in the hydrogen form and had an exchange capacity of 5.03 milliequivalents per gram of air-dried resin. This was converted to the ammonium form by several alternate cycles and recycles with 5 *M* HCl and 5 *M* NH_4Cl, the final NH_4Cl cycle being continued until the *p*H of the effluent equalled the *p*H of the influent. The resin was then treated with 0.15 *M* NH_4Cl until the *p*H of the effluent equalled that of the influent, washed several times with distilled water until the effluent gave no test for chloride ion, and finally air-dried. The 40–60 mesh screening fraction, having a moisture content of 9%, was used throughout this investigation.

Procedure.—Twenty 5-ml. volumes containing the indicated concentrations of beryllium salt (to each of which was added a known amount of radioactive Be^7 tracer) and ammonium perchlorate were adjusted to the desired *p*H with a measured volume of standardized ammonium hydroxide. A Beckman Model G *p*H meter was employed for these adjustments. Twenty milliliters of each solution was then pipetted into a 50-ml. glass-stoppered erlenmeyer flask containing 0.070 g. (known in each case to the fourth decimal place) of ammonium resin. The unused portion of each solution was kept to be used as the standard in the final counting procedure. Each glass stopper was sealed with paraffin. The stopper and neck of each flask was finally wrapped tightly with Parafilm. The flasks were shaken for about 15 hours (*i.e.*, overnight) on a Boerner oscillating platform shaker in a constant temperature room maintained at 37°. After being shaken, the solutions were decanted

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[1] This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York.

[2] J. Schubert, *J. Phys. Colloid Chem.*, **52**, 340 (1948).

[3] I. Feldman, J. R. Havill and W. F. Neuman, to be submitted.

[4] (a) M. Prytz, *Z. anorg. allgem. Chem.*, **180**, 355 (1929); (b) **231**, 238 (1937); (c) W. Heukeshoven and A. Winkel, *ibid.*, **213**, 1 (1933); (d) J. Fauchierre and R. Schaal, *Compt. rend.*, **225**, 118 (1947).

[5] The results of the titrations past *p*H 4.6 are of no interest here because the ion-exchange studies, with which the titrations are correlated, gave erratic results above *p*H 4.6.

[6] J. Schubert and E. E. Conn, *Nucleonics*, Vol. 4, No. 6, 2 (1949).

[7] G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, New York, N. Y., 1949, p. 118.

[8] A. L. Underwood and W. F. Neuman, *Anal. Chem.*, **21**, 1348 (1949).

from the resin, and the pH's and beryllium concentrations were determined. The results were the same as after a 3-hour shaking period, indicating that the systems studied were at equilibrium.

Counting Procedure.—Relative beryllium concentrations were determined by gamma-ray counting, each solution containing radioactive tracer, Be^7. A standard scaling circuit equipped with a dipping Geiger–Muller tube[9] was used for the radioactive assays. The capacity of the cup was 3 ml. The counting chamber was enclosed with two-inch lead and contained a thermometer. Just previous to counting a solution the corresponding standard (*i.e.*, the portion of the original solution which had not been in contact with resin) was counted. This procedure minimized errors due to dilution during the pH adjustment and to temperature effects on the counting tube.

It is believed that the total experimental error for each experiment was about 2%. This corresponds to an error in K_d varying from 2.5 to 10% as the ionic strength is increased from 0.1 to 0.4.

pH Titrations.—The data presented in Table I were obtained by titrating 25-ml. volumes of the indicated beryllium sulfate solutions with CO_2-free sodium hydroxide under a nitrogen atmosphere until the pH reached 4.6. Because of the sodium perchlorate present the ionic strength of each solution after titration to pH 4.6 was about 0.11. The solution which was 3.37×10^{-4} M in beryllium sulfate had, of course, an ionic strength of 0.10.

The "% Be hydrolyzed" was calculated by means of the equation

$$\% \text{ Be hydrolyzed} = \frac{\text{moles NaOH added} + C_{H^+}V}{\text{moles BeSO}_4\text{ added}} \times 100\%$$

This equation follows from the fact that titrations of beryllium sulfate, in the range 0.005 to 0.1 M, show an inflection point when one equivalent of sodium hydroxide is added for each equivalent of beryllium titrated.[4a] The hydrogen ion concentration in moles/liter, C_{H^+}, at pH 4.6, was obtained by assuming a value of 0.8 for the activity coefficient of the hydrogen ion. This value was obtained from the activity coefficient of hydrochloric acid[10] by applying the MacInnes individual ion activity coefficient concept,[11] *i.e.* $\gamma_{H^+} = \gamma^2_{HCl}/\gamma_{KCl}$. The symbol V represents volume in liters of the solution at pH 4.6.

Results and Discussion

The ion-exchange reaction between beryllium ions and the ammonium form of Dowex 50 resin may be expressed as

$$Be^{++} + 2NH_4R \longrightarrow BeR_2 + 2NH_4^+$$

where R refers to the anionic part of the resin. The thermodynamic equilibrium constant for this reaction is

$$K_T = \frac{(BeR_2)(NH_4^+)^2}{(Be^{++})(NH_4R)^2} \qquad (1)$$

the quantities in the parentheses representing activities.

As long as the mole fraction of BeR_2 is very small compared to that of NH_4R, one may assume that the activity coefficient ratio, $\gamma_{BeR_2}/\gamma^2_{NH_4R}$, of the two resin forms is independent of the ionic strength of the liquid phase and remains constant even when (BeR_2) varies.[12] In addition, the concentration of NH_4R does not undergo significant change. Under these conditions, the exchange reaction will satisfy the following constant, K_0.[14]

$$K_0 = \frac{N_{BeR_2}\,\gamma^2_{NH_4^+}\,C^2_{NH_4^+}}{N_{NH_4R}\,\gamma_{Be^{++}}\,C_{Be^{++}}} \qquad (2)$$

where N, γ and C refer to the number of moles, the activity coefficient, and the molar concentration, respectively, of the substances indicated by the formulas in the subscripts.

If Schubert's definition[15] for the distribution coefficient, K_d, is employed, then for this system

$$K_d = \frac{\%\text{ Be on resin}}{\%\text{ Be in solution}} \times \frac{\text{volume of solution}}{\text{mass of resin}} \qquad (3)$$

If the volume/mass ratio is kept constant, K_d is proportional to $N_{BeR_2}/C_{Be^{++}}$. Incorporating K_d into equation (2) gives equation (4), containing a new constant, K.

$$K\gamma_{Be^{++}} = K_d\gamma^2_{NH_4^+}C^2_{NH_4^+}{}^{16} \qquad (4)$$

For an aqueous solution containing only beryllium and ammonium perchlorates in such concentrations that $C_{Be^{++}} \ll C_{NH_4^+}$, the coefficient $\gamma_{NH_4^+}$ has the same value as in a pure solution of ammonium perchlorate of the same concentration as the mixture. As pointed out by Schubert,[17] equation (4) could be utilized to determine absolute values for activity coefficients if experiments could be conducted at sufficiently small concentrations of ammonium ion to allow extrapolation of the data to zero ionic strength, since K is constant by theory. Connick and Mayer,[18] however, found for the cerous ion that there is a lower limit of 0.4 to the ionic strength which can be studied accurately by this method, because at lower ionic strength nearly all the cerium is taken up by the resin. They, therefore, could determine only relative activity coefficient values For the same reason, we did not conduct experiments with beryllium at an ionic strength below 0.1.

In Fig. 1 are shown the values of $K_d\gamma^2_{NH_4^+}C^2_{NH_4^+}$ obtained when various solutions of beryllium in ammonium perchlorate were equilibrated with the ammonium form of Dowex 50 resin at 37°. The effects of varying beryllium concentration, of pH, and of the ammonium perchlorate concentration were studied. The ammonium ion activity coefficients used were calculated from the mean activity coefficients of ammonium chloride[19] and potassium chloride[20] at 25° by the MacInnes individual ion activity coefficient concept; *i.e.*, $\gamma_{NH_4^+} = \gamma^2_{NH_4Cl}/\gamma_{KCl}$. The temperature effect from 25 to 37° on the activity coefficient was considered to be insignificant for this work.

At pH 2.6, where beryllium exists as Be^{++}, solutions containing a beryllium concentration of about 10^{-9} M (carrier-free, radioactive tracer concentra-

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[9] A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1946, p. 1266.

[10] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950.

[11] D. A. MacInnes, THIS JOURNAL, **41**, 1086 (1919).

[12] The data of Lowen, *et al.*,[13] can be interpreted to show that, for the exchange of divalent ions, M^{++}, with the monovalent cations of a resin, NR, the activity coefficient ratio $\gamma_{MR_2}/\gamma^2_{NR}$ changes less than 5% when the mole fraction of MR_2 is increased from zero to 0.05.

[13] W. K. Lowen, R. W. Stoenner, W. J. Argersinger, Jr., A. W. Davidson and D. N. Hume, THIS JOURNAL, **73**, 2673 (1951).

[14] G. E. Boyd, J. Schubert and A. W. Adamson, *ibid.*, **69**, 2828 (1947).

[15] J. Schubert, E. R. Russell and L. S. Myers, Jr., *J. Biol. Chem.*, **185**, 387 (1950).

[16] Individual ion activity coefficients such as $\gamma_{Be^{++}}$ and $\gamma_{NH_4^+}$ are, of course, hypothetical quantities. Approximate values, however, can be calculated by the MacInnes concept[11] and can be used for the sake of simplicity where great accuracy is not claimed.

[17] J. Schubert, *J. Phys. Colloid Chem.*, **52**, 346 (1948); THIS JOURNAL, **73**, 4488 (1951).

[18] R. E. Connick and S. W. Mayer, *ibid.*, **73**, 1176 (1951).

[19] J. N. Pearce and G. G. Pumplin, *ibid.*, **59**, 1219 (1937).

[20] Reference 10, p. 369.

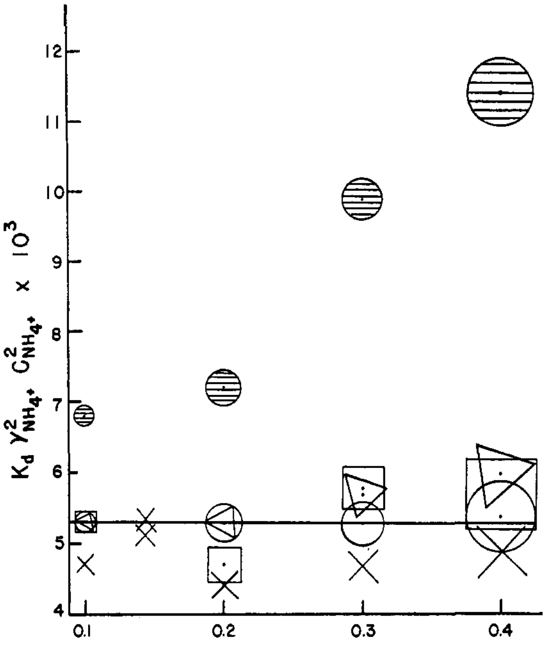

Fig. 1.—Variation of $K_d\gamma^2_{NH_4^+}C^2_{NH_4^+}$ with ammonium perchlorate concentration. The size of each point represents an experimental error of 2%: O, 10^{-9} M Be at pH 2.6; ∇, 3.6 × 10^{-4} M Be at pH 2.6; ×, 10^{-9} M Be at pH 4.6; □, 0.9 × 10^{-6} M Be at pH 4.6; ⊜, 3.6 × 10^{-4} M Be at pH 4.6. Each solution contained approximately 10^{-4} M chloride ion from the addition of the isotope which was supplied in dilute hydrochloric acid solution.

tion) and ammonium perchlorate concentration ranging from 0.1 to 0.4 M at 37° gave a constant value of 5.32 ± 0.05 × 10^{-3} for $K_d\gamma^2_{NH_4^+}C^2_{NH_4^+}$. Since K is a constant, then by equation (4) the value of $\gamma_{Be^{++}}$ is constant under these conditions.

When the initial beryllium concentration was raised to 3.6 × 10^{-4} M, the average value obtained for $K_d\gamma^2_{NH_4^+}C^2_{NH_4^+}$ was 5.6 ± 0.3 × 10^{-3}, in good agreement with the above constant. A slight trend in these data is observed ($K_d\gamma^2_{NH_4^+}C^2_{NH_4^+}$ increases from 5.3 to 6.0 × 10^{-3} as $C_{NH_4^+}$ increases from 0.1 to 0.4 M), but the variation is within experimental error.

In accordance with the views of other workers[5,13] when factors such as pH, beryllium concentration, or ammonium concentration are varied, the appearance of a significant amount of a beryllium species other than the Be^{++} ion would be detected by a change in the product $K_d\gamma^2_{NH_4^+}C^2_{NH_4^+}$. This quantity should increase at any given ionic strength if radiocolloids or polymeric ions are formed with charges equal to or greater than that of a Be^{++} ion, and should decrease if only simple hydrolysis to $BeOH^+$ occurs. Furthermore, if more than one polymeric species is formed the distribution of species should depend upon the ionic strength, and $K_d\gamma^2_{NH_4^+}C^2_{NH_4^+}$ should vary with changing ionic strength.

At pH 4.6 K_d was still inversely proportional to the square of the activity of the ammonium ion when the initial beryllium concentration was within the range 10^{-9} to 10^{-6} M. At 10^{-9} M beryllium concentration the constant obtained was 4.9 ± 0.3 × 10^{-3}. At 0.9 × 10^{-6} M beryllium it was 5.4 ± 0.4 × 10^{-3}. These values seem sufficiently close to that of $K\gamma_{Be^{++}}$ at pH 2.6 to indicate that at pH 4.6 and in the beryllium concentration range 10^{-9} M to 10^{-6} M most of the beryllium is still in an unhydrolyzed monomer state.

When, however, solutions containing 3.6 × 10^{-4} M beryllium perchlorate and ammonium perchlorate ranging from 0.1 to 0.4 M were raised to pH 4.6 and equilibrated with the ammonium resin, the product $K_d\gamma^2_{NH_4^+}C^2_{NH_4^+}$ did not remain constant as the ammonium ion concentration was varied. Furthermore, throughout the entire ammonium concentration range studied the value of $K_d\cdot\gamma^2_{NH_4^+}C^2_{NH_4^+}$ was considerably higher, 6.8 × 10^{-3} to 11.4 × 10^{-3}, than the values obtained in the previous studies. These facts indicate that at a beryllium concentration of 3.6 × 10^{-4} M and at pH 4.6 a significant amount of beryllium had been hydrolyzed and had polymerized. The results can not be attributed to changes in the activity coefficients in the solid phase, because the mole fraction of the beryllium resin is still quite small, < 0.02.

A striking presentation of the conditions under which polymerization begins is given by Fig. 2. Polymerization at pH 4.5 and an ionic strength of 0.1 seems to begin when the beryllium concentration reaches 10^{-5} M, in agreement with the pH data of Table I. The sudden decrease in K_d when the beryllium concentration is raised above 10^{-3} M could be due to the lack of ideality of the solid phase,[12] for the mole fraction of the beryllium resin form indicated by the K_d value increases from *ca.* 0.046 at 10^{-3} M beryllium to *ca.* 0.36 at 10^{-2} M beryllium.

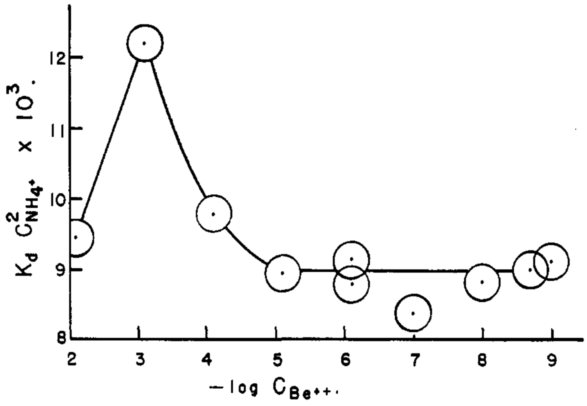

Fig. 2.—Variation of $K_d\ C^2_{NH_4^+}$ with beryllium concentration in approximately 0.1 M ammonium perchlorate and at a pH of 4.5 ± 0.08. Each solution contained approximately 10^{-4} M chloride ion from the addition of the isotope which was supplied in dilute hydrochloric acid solution. (The drop in pH to 4.28 of the 10^{-2} M beryllium solution after equilibration with resin indicates that our NH_4R resin contained about 0.2% of the hydrogen form, HR. This would have no significant effect on any of the interpretations of this paper.)

Studies at a higher pH were not feasible, since even in tracer concentration, 10^{-9} M, at pH 5.5 beryllium did not remain completely in solution, as shown by a significantly decreased gamma-count for solutions which had *not* been in contact with resin.

A quantitative interpretation of the state of polymerization represented by the shaded circles in Fig. 1 did not seem justified because it would have involved several assumptions unwarranted at the present time.

The authors wish to acknowledge the assistance of Dr. John Bonner and Mr. Robert Vosteen for assembling and maintaining the counting equipment.

ROCHESTER 20, NEW YORK RECEIVED AUGUST 31, 1951

CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF THE DEPARTMENT OF CHEMISTRY OF HARVARD UNIVERSITY]

Boron–Nitrogen Systems. I. Dimethylaminoboron Dichloride[1,2]

BY CHARLES A. BROWN[3] AND ROBERT C. OSTHOFF[4]

Some physical and chemical properties of monomeric and dimeric dimethylaminoboron dichloride are reported. The monomer reacts quantitatively with trimethylamine and hydrogen chloride to form one-to-one addition compounds. Some physical properties of these addition compounds are given. The trimethylamine adduct reacts with hydrogen chloride to yield trimethylamine hydrochloride and monomer hydrochloride. Thermal decomposition of the amine adduct yields $Cl_3B:N(CH_3)_3$, $[(CH_3)_2N]_3B$ and trimethylamine. Measurement of the dipole moment of dimeric dimethylaminoboron dichloride leads to the assignment of a cyclic structure consisting of a four-membered ring of alternate boron and nitrogen atoms.

I. Introduction

The bonds between boron and nitrogen atoms present two extremes in type. In one case the nitrogen atom donates a pair of electrons to boron with the formation of a coördinate covalent or donor–acceptor complex. The second possibility is the formation of a "normal" covalent bond between these two atoms. Bonds intermediate between these extremes, *i.e.*, contribution of both types to the resonance hybrid, probably account for the shortening of the boron–nitrogen distance in such compounds as boron nitride, borazole ($B_3N_3H_6$) and some of its derivatives.[5]

Although a large number of studies have been published concerning the properties of coördinate covalent boron–nitrogen systems,[6,7] the character of the normal covalent bond and the intermediate bond types deserves a more detailed investigation. This paper is the first of a series directed toward the properties of some simple compounds which illustrate these types of bonding.

Experimental

II. Monomeric Dimethylaminoboron Dichloride

Preparation.—The monomer was prepared in a manner similar to that which has been described by Wiberg and Schuster.[8] Anhydrous dimethylamine (Eastman Kodak Co. "White Label") was added without further purification to boron trichloride at liquid nitrogen temperatures. The reaction mixture was allowed to warm slowly to room temperature and the volatile products fractionated by means of traps maintained at −20, −80 and −196°. The pure product, which was collected in the trap at −80°, was stored in an evacuated bulb at Dry Ice temperature until used.

The best yields of monomeric dimethylaminoboron dichloride (35% based upon the amount of dimethylamine employed) were obtained at a mole ratio $[BCl_3/HN(CH_3)_2]$ of 0.72. Although the equation

$$BCl_3 + 2HN(CH_3)_2 \longrightarrow (CH_3)_2NBCl_2 + (CH_3)_2NH{\cdot}HCl$$

was used in the calculation of yields, the formation of the hydrogen chloride adduct of the monomer and higher substitution products of boron trichloride, *i.e.*, bis-dimethylaminoboron chloride and tris-dimethylaminoboron, probably account for the low yields.

The purity of the monomer was checked by a determination of the melting point (obsd. −43°; previous value, −46°); the entire vapor pressure curve gave excellent agreement with the previously reported values.[8] Measurements of vapor density of monomeric dimethylaminoboron dichloride gave a value of the molecular weight in the vapor phase of 129 at 25°; calcd., 125.8.

When monomeric dimethylaminoboron dichloride is allowed to stand at room temperature for a period of several days, a crystalline solid dimeric modification forms. This dimer was first described by Wiberg and Schuster[9] and a more complete description of its properties is given below. However, the dimerization reaction is suppressed at low temperatures, and it is possible to store the monomer at −80° *in vacuo* for a period of several weeks.

Density of Liquid Monomer.—Densities of liquid monomer were evaluated by means of a pycnometric method. A 2-ml. dilatometric pycnometer was constructed with a stem of Tru-bore Pyrex tubing. The volume was carefully calibrated with mercury and the volume change per unit stem length determined. A sample of monomer was distilled into the pycnometer and sealed off. The pycnometer was then placed in a constant temperature bath and the level of the liquid monomer in the capillary determined by means of a cathetometer.

The results which were obtained from two independent samples are summarized in Table I. The analytical expression for the density as a function of Centigrade temperature in the range −40 to 22° is

$$d = 1.1629 - 0.001177t$$

with an average deviation of 0.0008.

Surface Tension and Parachor.—Surface tensions were determined with the liquid monomer under its own vapor pressure by the application of the method of Mills and Robinson.[10] In Table I the data obtained from two independent samples in the temperature range −40 to 35° are summarized along with the observed parachor at each temperature. The equation representing the surface tension as a function of temperature in °C. is

$$\gamma = 29.24 - 0.1238t \text{ (dynes per cm.)}$$

with a mean deviation of 0.02. The measurement of density and surface tension above room temperature leads to less reliable results since the liquid monomer slowly dimerizes to solid $[(CH_3)_2NBCl_2]_2$. The rate of the dimerization increases as the temperature is increased up to at least 80°.

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(1) Presented before the Division of Physical and Inorganic Chemistry, American Chemical Society Meeting, Chicago, Ill., September 4, 1950.

(2) In part taken from the Ph.D. Thesis of Robert C. Osthoff, Harvard University, 1951.

(3) Department of Chemistry, Western Reserve University, Cleveland 6, Ohio.

(4) Procter and Gamble Fellow in Chemistry, Harvard University, 1951.

(5) S. H. Bauer, *Chem. Revs.*, **31**, 43 (1940).

(6) A. W. Laubengayer and G. F. Condike, THIS JOURNAL, **70**, 2274 (1948).

(7) D. R. Martin, *Chem. Revs.*, **34**, 461 (1944).

(8) E. Wiberg and K. Schuster, *Z. anorg. Chem.*, **213**, 77 (1933).

(9) E. Wiberg and K. Schuster, *ibid.*, **213**, 89 (1933).

(10) H. Mills and P. L. Robinson, *J. Chem. Soc.*, 1823 (1927).