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RESEARCH MEMORANDUM

A METHOD FOR DETERMINING THE COMPOSITION OF

METHANOL - TRIMETHYL BORATE MIXTURES

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS
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A METHOD FOR DETERMINING THE COMPOSITION OF

METHANOL - TRIMETHYL BORATE MIXTURES

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SUMMARY

A method was developed for rapidly determining the composition of
methanol - trimethyl borate mixtures. Pure methanol and trimethyl borate
were prepared, and their properties were accurately determined. The
densities and refractive indices of several mixtures of these compounds
were determined. Analysis of the curves obtained showed that greater
accuracy in determining the composition was possible from a density de-
termination. The compositions of the mixtures prepared were checked
potentiometrically using precautions necessary for accurate results.
The accuracies of the analytical techniques are discussed.

INTRODUCTION

During an investigation of reactions of trimethyl borate, a simple
rapid method for determining the composition of methanol - trimethyl
borate mixtures was desired. A method based on physical properties was
considered to be most suitable. The literature, however, disclosed con-
siderable disagreement (refs. 1 to 12) as to the properties of trimethyl
borate and its azeotrope with methanol.

An investigation was therefore undertaken at the NACA Lewis labora-
tory to determine: (1) the properties of trimethyl borate of known
purity, (2) the properties and composition of the methanol - trimethyl
borate azeotrope, and (3) the applicability of refractive index and
density in determining the composition of methanol - trimethyl borate
mixtures. A method based on the change in density with composition was
found to give analyses of sufficient accuracy.

EXPERIMENTAL DETAILS

Materials

Methanol. - Commercial methanol was purified by treatment with sodium hydroxide followed by fractional distillation in a 6-foot Podbielniak column operated at an efficiency rating equivalent to about 100 theoretical plates. In order to ensure accurate data by preventing contamination with moisture, all manipulations were performed in a closed system or in a dry box made inert with nitrogen. The properties of the purified methanol agreed with the best values given in the International Critical Tables.

Methanol - trimethyl borate azeotrope. - The crude ester was obtained from a commercial source labeled as a 70 - 30 mixture by weight of ester and methanol. It was purified by distillation in the Podbielniak column described in the preceding paragraph and was stored and handled in a dry box to protect it from hydrolysis.

Trimethyl borate. - The azeotrope consisting of trimethyl borate and methanol was broken by treating it with lithium chloride, as described in reference 11. The trimethyl borate was then purified by fractional distillation under nitrogen atmosphere in the Podbielniak column.

The purity of the ester was determined by calculation (ref. 13) as follows: The freezing point and the freezing point for zero impurity were obtained by analysis of the freezing curve; the heat of fusion was determined to be 1993 calories per mole. From these data, the purity of the sample was determined to be 99.92 mole percent.

The infrared spectrum of trimethyl borate, which is not presented herein, was essentially the same as that recorded by Samuel P. Sadtler & Son Inc., Phil. (Pa.), except for a band which appeared in their spectrum at 3.0 to 3.1 microns. The presence of this band in their spectrum was undoubtedly caused by a hydroxyl impurity from methanol in their sample.

Properties

Density. - The densities were determined, unless otherwise noted, at 20.0° ±0.1° C with a calibrated Sprengel type pycnometer (ref. 14). The average deviation for these determinations was 0.0002 unit.

Index of refraction. - The indices of refraction were measured at 20.0° ±0.1° C with a Bausch and Lomb Abbé 56 refractometer. The instrument was installed in a dry box made inert with nitrogen, and all measurements were made under these conditions.

Freezing point. - The thermometric system consisted of a platinum resistance thermometer, a Mueller type G-2 resistance bridge, and a highly sensitive galvanometer. This apparatus is the same as is commonly used with the standard technique (ref. 13). The freezing tube itself, however, contained a helical solenoid-operated, reciprocating stirrer and was charged with 10 milliliters of sample in a dry box. The tube was then sealed and the freezing point determined in the usual manner.

Boiling point. - The boiling points were determined in an ebulliometer equipped with apparatus of the same type as was used for the determination of the freezing point. The measurements were made in a nitrogen atmosphere at a pressure of 760 millimeters of mercury with an accuracy of ±0.05° C.

Infrared spectrum. - The infrared spectra were obtained on a Baird double-beam recording spectrophotometer with a 0.1-millimeter sodium chloride cell, which was filled in a dry box.

Heat of fusion. - The heat of fusion was determined in a nitrogen atmosphere by the method of reference 15. In this method, several samples with known heats of fusion are frozen under standardized conditions in a vacuum-jacketed tube. The rate of heat transfer at the various temperature gradients is then measured to give a calibration curve for the tube. Knowing the rate of heat transfer and the temperature gradient, the heat of fusion can be calculated for an unknown compound when it is frozen under the same standardized conditions.

Procedure

The pure materials, methanol and trimethyl borate, were placed in a dry box purged with nitrogen. A series of eight compositions by weight, accurate to ±0.1 milligram, were prepared and stored in carefully stoppered bottles. The bottles were opened only in a nitrogen atmosphere in which the measuring instruments were located. The refractive index and density were determined for each composition under these conditions. The density and refractive index of the highly purified azeotrope were also determined.

RESULTS AND DISCUSSION

Table I shows the methanol - trimethyl borate data plotted in figures 1 and 2 as density and refractive index, respectively, against concentration of trimethyl borate. These curves show definite curvature as compared with the straight lines obtained in reference 7. In table II are listed the physical properties obtained for pure trimethyl borate and the methanol - trimethyl borate azeotrope and, for comparison, some

of the properties reported previously in the literature. The equations obtained by the least-squares method for the curves shown in figures 1 and 2, respectively, are

$$d_4^{20} = 0.7912 + 0.1199 \times 10^{-2}x + 0.2141 \times 10^{-5}x^2$$

and

$$n_D^{20} = 1.3285 + 0.2584 \times 10^{-3}x + 0.3123 \times 10^{-6}x^2$$

where x is the percent by weight of trimethyl borate.

The density of the azeotrope was determined, and its composition was calculated from the density equation to be 74.86 percent trimethyl borate and 25.14 percent methanol. This compares with 75.5 and 24.5 percent, respectively, reported in reference 11.

The composition of the azeotrope which is shown to fall on the curve was checked independently by titrating the boric acid formed on hydrolysis of the mixture. The titration was done with a Beckman Model G pH meter with mannitol used as the activator. The values coincided only after the principles expressed by Schäfer (ref. 16) were applied.

Schäfer showed that the pH at the beginning and end of the titration curve of H_3BO_3 with alkali depended on the amount of mannitol used as activator. The volume of alkali required to reach the equivalence point did not change, of course. Therefore, when a particular pH was used as the criterion for the end point, the value for equivalence changed with the amount of mannitol used.

In some reported procedures the boric acid is arbitrarily titrated between some initial fixed pH value and a final value. The adjustment of the initial pH is necessary if the boric acid is to be determined in the presence of strong acids. However, when H_3BO_3 alone is present, this technique is obviously incorrect since an amount of boric acid, depending on its concentration, will thereby be neutralized. This error can amount to several tenths of a percent of boron.

In order to titrate boric acid with an accuracy of at least 0.1 percent, therefore, the following variables must be fixed: (1) the amount of mannitol used as activator, (2) the pH range over which the titration is performed, and (3) the relative concentration of boron to be titrated. An evaluation of the reliable methods reported for this determination of boron (ref. 17) showed that the procedures which use these principles either inadvertently or by design do yield correct values.

A final important correction which must be applied in the analyses is one which accounts for the pH of the distilled water used for

hydrolysis and as a solvent. The pH of the distilled water at this laboratory varied at different times from 5.7 to 6.4. The results reported, however, are corrected for water at pH 7.

Further confirmation of the composition of the azeotrope was obtained by treating it as a pure substance of determined composition. The azeotrope was mixed with pure trimethyl borate. The densities of these trimethyl borate - trimethyl borate azeotrope mixtures fell on the same curve as before.

The relation of both density and refractive index to composition shows very slight deviations from linearity. The change in density can be read to ±0.0002 gram per milliliter, which represents a ±0.13-percent change in composition. The change in refractive index can be read to about ±0.0002, which represents a maximum of about ±0.68-percent change in composition. It can be seen, therefore, that the determination of density can be about five times as accurate for the estimation of composition as the refractive-index determination. It is therefore more applicable to the problem than the refractive-index determination, though the latter is faster.

An assumption involved in this work is that the mixture is reasonably free of contaminants which could affect the results. The purity of the material studied was proven by analysis. This assumption for most samples of methanol - trimethyl borate is not unreasonable in view of the method of synthesis, which involves simply the reaction of boric oxide with methanol

$$B_2O_3 + 6CH_3OH \rightarrow 2B(OCH_3)_3 + 3H_2O$$
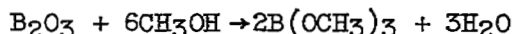
or a set of reactions equivalent to the equation as written. Although excess boric acid precipitates out on hydrolysis, hydrolytic decomposition may affect the results because of the solubility of boric acid in the liquids.

Lewis Flight Propulsion Laboratory
    National Advisory Committee for Aeronautics
        Cleveland, Ohio, August 17, 1955

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TABLE I. - DENSITY AND REFRACTIVE INDEX OF

METHANOL - TRIMETHYL BORATE MIXTURES

Concentration of trimethyl borate, percent by weight	Density at 20° C	Refractive index, n_D^{20}
0	0.7912	1.3286
19.71	.8157	1.3337
39.84	.8424	1.3392
54.93	.8637	1.3436
67.06	.8812	1.3470
70.12	.8859	1.3485
72.71	.8895	1.3492
79.95	.9010	1.3512
90.09	.9164	1.3543
100.00	.9327	1.3574

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TABLE II. - PHYSICAL PROPERTIES OF TRIMETHYL BORATE AND THE METHANOL AZEOTROPE

Material	Freezing point, °C	Boiling point, °C	Density, d_4^{20} (a)	Refractive index, n_D^{20}	Heat of fusion, cal/mole	Composition of trimethyl borate, percent by weight
Trimethyl borate	-28.313 [d]-28.47 [g]-29.3±0.1 [l]-34	[b]55-56 [e]65 [h]67.5-68.5/750mm [j]68.5 68.86/760mm [k]68	[c]0.916[30] [b].919 .9198[30] [k].925[25/15] [c,l,m].928 [f].932 .9327 [n].9502	1.3574 [f]1.3558 [h]1.3488	1993 [d]2643	
Trimethyl borate - methanol azeotrope		54.41 [o,h]54.6 [k]54-56	0.8930 .8810[30] [k].892[25/15]	1.3494 [k]1.354		[n]30 [o]68 74.86 [e]75.1 [h]75.5

[a]Except as noted.
[b]Ref. 2.
[c]Ref. 8.
[d]Ref. 10.
[e]Ref. 12.
[f]Ref. 4.
[g]Ref. 6.
[h]Ref. 11.

[i]Ref. 5.
[j]Ref. 14.
[k]Ref. 7.
[l]Ref. 9.
[m]Ref. 9 gives the equation $d(g/ml) = 1.3018 - 1.2667 \times 10^{-3} T$ valid from 23° to 29° C.
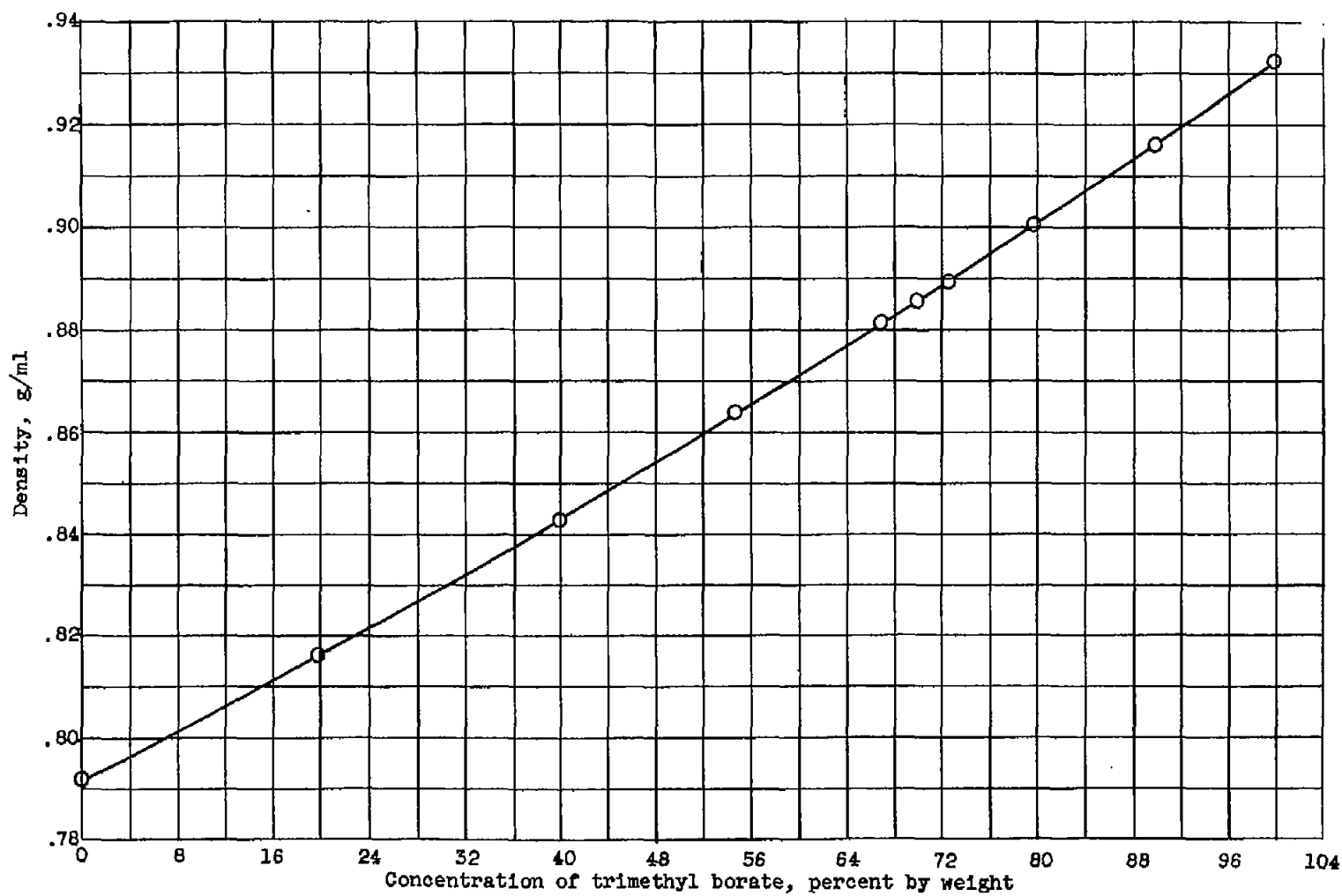[n]Ref. 1.
[o]Ref. 3.

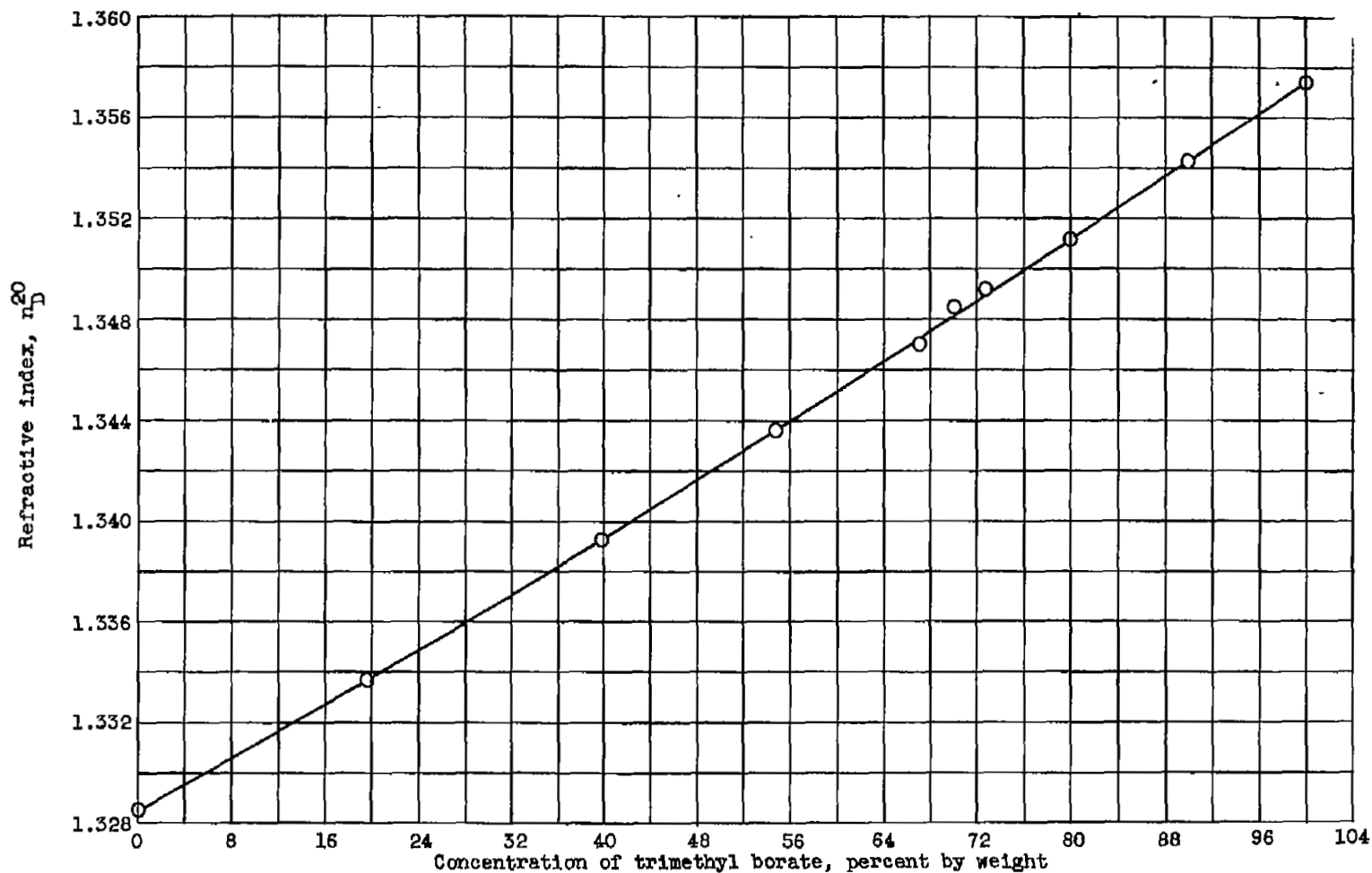Figure 1. – Density of methanol – trimethyl borate mixtures.

Figure 2. - Refractive index of methanol - trimethyl borate mixtures.