[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

The Absorption Spectra of Cobaltous Compounds. IV. The Alkali Oxide–Boric Oxide Glasses

BY WALLACE R. BRODE

A spectroscopic examination of commercial samples of blue cobalt glasses shows that their absorption spectra are by no means identical (Fig. 1). This fact has been noted in the literature,[1,2,3] but, beyond the inference that the constitution of the glass will determine the characteristics of the absorption spectra, there are very few specific data on the cause of the blue color in cobalt glasses and glazes or the reasons why their absorption spectra will give bands with different relative intensities.

Since even the simplest of the commercial glasses contain the oxides of many elements it was felt best to avoid such combinations and confine the preliminary experiments to two component systems, in an attempt to determine the effective component and the nature of the cobalt complex that produced the color. As might have been predicted the two component systems had a marked tendency to form crystalline compounds instead of amorphous glasses. In time it is hoped that a large series of basic oxide–acidic oxide glasses can be studied, including systems with more than two component compounds and the substitution of oxygen with halogens, sulfur or other elements. The system chosen for the preliminary study of cobalt colored glasses was that of the alkali oxides with boric oxide. This system includes the borax bead which is used in the qualitative detection of cobalt.

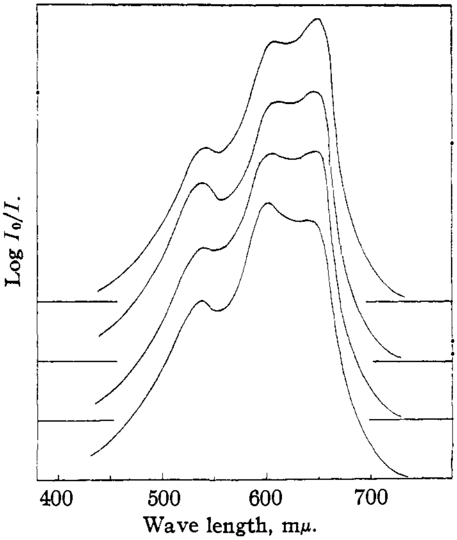

Fig. 1.—The absorption spectra of four typical samples of blue cobalt glasses. The upper curve is characteristic of potash glasses while the lower curve is characteristic of soda glasses.

A study of the absorption spectra of cobaltous hydroxide, dissolved in concentrated aqueous alkali hydroxide solutions, by Dr. R. A. Morton and

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(1) Fedotieff, *Z. anorg. allgem. Chem.*, **134**, 87 (1924).

(2) Zsigmondy, *Ann. Physik*, **4**, 60 (1901).

(3) Gibson and co-workers, Technologic Papers of the Bur. Standards, No. 148 (1920), Scientific Papers of the Bur. Standards, No. 547 (1927).

the author[4] at the University of Liverpool, showed that a slight change in intensity of the absorption bands, without a change in wave length, would be expected with a change from NaOH to KOH. The data presented in this paper would confirm this effect and indicate that the cobalt color in concentrated aqueous alkali hydroxide is the same as in the alkali oxide glasses.

In earlier papers of this series[5] it has been shown that a change from Cl, to Br, to I in the complex causes a marked increase in wave length of the absorption band with an increase in the molecular weight. The conclusion was drawn that these elements must be directly connected with the chromophore, since their mass influences the frequency of vibration of the chromophoric group. In this paper a new type of effect is described, in which the change in elements, from Li to Na to K to Cs, causes no shift in the frequency of the band but rather a change in the band intensities. This latter effect is not of necessity due to a difference in mass and might arise from certain chemical differences such as a tendency to form polyvalent compounds, electromotive effects, etc. It would seem then that none of these alkali metals are directly connected to the chromophore yet they have a close relation with the cobalt such as might occur in a coördinated oxide formed from M_2O and CoO in which the metal would not be directly attached to the cobalt but its affinity for oxygen would determine the ease of formation of the coördinated cobalt oxide and the strain upon the cobalt–oxygen coupling. Such a theory would lead to the prediction of an easily formed and stable cobalt oxygen coördinated complex in the presence of Cs_2O and a difficultly formed and unstable complex with Li_2O. The experimental data in this paper are in accord with this theory.

In an earlier paper[5b] it was shown that the addition of halogen acids to a neutral pink solution of a cobaltous salt converted it to a blue-green solution. In this paper it is shown that the addition of alkali oxides to a pink cobalt glass of boric oxide converts the color to blue. These different absorption spectra should not be considered as derived from extreme acid and basic colors with the pink cobaltous colors as the neutral range. It is possible to add halogen salts to a blue cobalt glass and change the absorption bands to the blue-green system of the halogen acids without passing through any pink stage. It has been previously shown[5c] that a similar effect is observed with regard to the change from the blue pyridine–quinoline solutions to the halogen acid solutions. Strong acids such as sulfuric acid and nitric acid do not give blue solutions while neutral solvents such as ethyl alcohol, ethyl ether and acetone give blue solutions. The evidence points to an oxide coördinated system which differs only from the halogen system by replacement of the halogen with oxygen. The similarity of the

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(4) Then a Fellow of the John Simon Guggenheim Memorial Foundation.

(5) (a) Brode, *Proc. Roy. Soc.*, **118A**, 286 (1928); (b) Brode and Morton, *ibid.*, **120A**, 21 (1928); (c) Brode, THIS JOURNAL, **53**, 2457 (1931).

two systems is shown through the analogous shape of their absorption bands, the oxygen-system bands being of similar shape but shifted to a higher frequency, which would be expected as a result of the smaller mass of the oxygen as compared with the halogens, Cl, Br and I. In both the oxygen and halogen systems the colors can be shifted from pink to blue by an increase in temperature. The pink colors obtained are the same in all systems, while the blue colors vary depending on whether O, Cl, Br, I, S, SCN, pyridine, quinoline, etc., are combined with the cobalt.

In the alkali oxide–boric oxide glasses two different influences are considered, (a) the change in the ratio between the alkali oxide and boric oxide concentrations, and (b) the change of the alkali oxide from Li to Na, to K to Cs. Since pure boric oxide alone gave only the pink color, characteristic of the uncoördinated cobaltous compounds, it was felt that its action, like that of water in the halogen acid systems, was merely that of a solvent. There is another possible type of substitution in this series of glasses which should be quite convincing in showing which of the elements involved actually coördinate with the cobalt. This would involve the replacement of oxygen with other elements such as the halogens, sulfur, selenium and tellurium. Although glasses of this type will be discussed in a subsequent paper, the Na_2S–$2B_2S_3$ (thioborax) glass has already been prepared and the shifted position of the bands definitely confirms the theory that oxygen and sulfur are coördinated with cobalt in much the same manner as the halogens.

Preparation of Glasses and Method of Observation

The melts described in this paper were prepared, in unglazed Sillimanite crucibles, by thoroughly grinding and fusing to a clear liquid the weighed quantities of alkali carbonate, boric acid and cobalt carbonate. When completely fused each melt weighed between 10 and 15 g., of which the cobalt in the form of CoO formed about 0.1%. Melts with ratios of one mole of alkali oxide to two moles of boric oxide (M_2O–$2B_2O_3$) or lower boric oxide content, appreciably etched the crucibles and M_2O–B_2O_3 melts invariably went through the crucible in a short time. For this reason many of the glasses with a ratio of M_2O–$2.5B_2O_3$ or less boric oxide were subsequently prepared in platinum crucibles. These latter glasses gave absorption curves identical with those obtained from the glasses prepared in the Sillimanite crucibles, indicating that there was no apparent color effect due to the dissolving of small amounts of Al_2O_3 or SiO_2. All the cesium glasses were prepared in platinum crucibles.

For the absorption spectra observations, glass disks with nearly plane surfaces were prepared by the use of rings made of a single loop about 2 cm. in diameter on the end of a nichrome or platinum wire. In cases where extra thick glasses were desired two or three turns were used. A bead from the melt was formed on the wire loop of a size sufficient to produce a disk from 3 to 4 mm. thick. The disk was laid on a polished carbon block and the upper surface liquefied with a gas oxygen blow torch. The bead was then allowed to cool and when nearly solidified it was turned over and pressed lightly on the polished carbon block. The surface then uppermost was similarly treated and afterwards each was fire polished or flashed with the flame to remove slight roughness caused by the contact cooling with the carbon block. The resulting glasses were quite satisfactory for the measurement of their absorption spectra. In a few cases where there was a marked tendency to crystallize it was necessary to form the disk by rapid cooling and no fire polishing was possible. The method used in such cases was to pour out a puddle of the melt on a polished stone surface and freeze it at once by pressing down on the top of this drop with a cold carbon block. All of the prepared disks were kept in an oven at 100° until observations on their absorption spectra and thickness could be made. This treatment effected a partial annealing and prevented the rapid formation of a film on the glasses due to the hydration of the boric oxide. A subsequent coating of collodion served to preserve the samples permanently.

The absorption spectra measurements were made on a Bausch and Lomb spectrophotometer. The data. in a graphic form, as presented in this paper have been recalculated to equivalent concentrations of cobalt and convenient thickness of sample. Several samples were prepared of certain alkali oxide–boric oxide melts with widely differing cobalt concentrations (varying from 0.04 to 2.5%). These gave nearly identical absorption spectra curves in thicknesses inversely proportional to the cobalt concentration and hence showed that there were no concentration effects within the ranges studied.

In the cases of those samples which could not be fire polished after pressing out, and of certain others which were partially crystallized, a necessary correction was made for the considerable diffusion and general absorption of light from the rough surfaces. This correction was made by subtracting the value of the absorption coefficient obtained at 730 $m\mu$ from all of the observed values. since it was shown in the clear samples and other glasses studied that there was no absorption at this point due to the cobalt color. Observation points have been omitted from the curves in this paper in order to permit a better visual comparison of the curves. Readings were made every 5 $m\mu$ from approximately 420 $m\mu$ to 730 $m\mu$, each plotted point being the average of several readings. Separate settings were made at each of the maxima, and additional data obtained for these points. The sample thicknesses and to some extent the concentrations increase as one goes from blue to pink glasses. The extinction coefficient for the blue glasses is about ten times that for a pink glass of the same thickness and concentration of cobalt. The solubility of cobalt oxide in boric oxide is very low so that some of this large drop in extinction coefficient may be due to a colloidal suspension of the cobaltous oxide in place of a true solution.

Discussion

Because of available data on the sodium oxide–boric oxide system the first glasses to be made were of this composition and more concentrations were considered in this series than in the subsequent alkali oxide glasses (Fig. 2). Ponomareff[6] has shown that there are eutectics in this system at Na_2O–$1.5B_2O_3$, Na_2O–$2.5B_2O_3$ and Na_2O–$3.5B_2O_3$ and that there are molecular compounds corresponding to Na_2O–B_2O_3, Na_2O–$2B_2O_3$, Na_2O–$3B_2O_3$ and Na_2O–$4B_2O_3$ but that beyond this last boric oxide concentration there does not appear to be a continuation of this series of eutectics and compounds. This might indicate that the maximum stable sodium borate was the octaborate, $Na_2B_8O_{13}$. In Fig. 2 it is noticeable that in this same neighborhood of Na_2O–$4B_2O_3$ the change takes place between the pink and blue glasses. This color change does not take place at a fixed concentration ratio of sodium oxide to boric oxide but rather occurs over a given concentration range. This range may be shifted to higher or

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(6) Ponomareff, *Z. anorg. Chem.*, **89**, 390 (1914).

lower alkali oxide concentrations by a change in temperature. At high temperatures large amounts of boric oxide are required to produce a pink coloration, while at low temperatures, especially with liquid air, only a very small amount of boric oxide is necessary to produce a pink color. It is quite possible that a study of the stability of these various sodium oxide–boric oxide compounds at other temperatures would show a similar variation as the temperature color change. The change from pink to blue is not a shift of the frequency of the absorption band but rather the loss of intensity in one band concomitant with the gain of intensity of other bands, similar to the conditions in an indicator color change.[7] Glasses within this equilibrium range will show these bands and hence the resultant curve should be capable of analysis into component curves, providing an intermediate is not formed.[8] Subtraction of either the extreme blue or pink curves from the equilibrium curves indicates

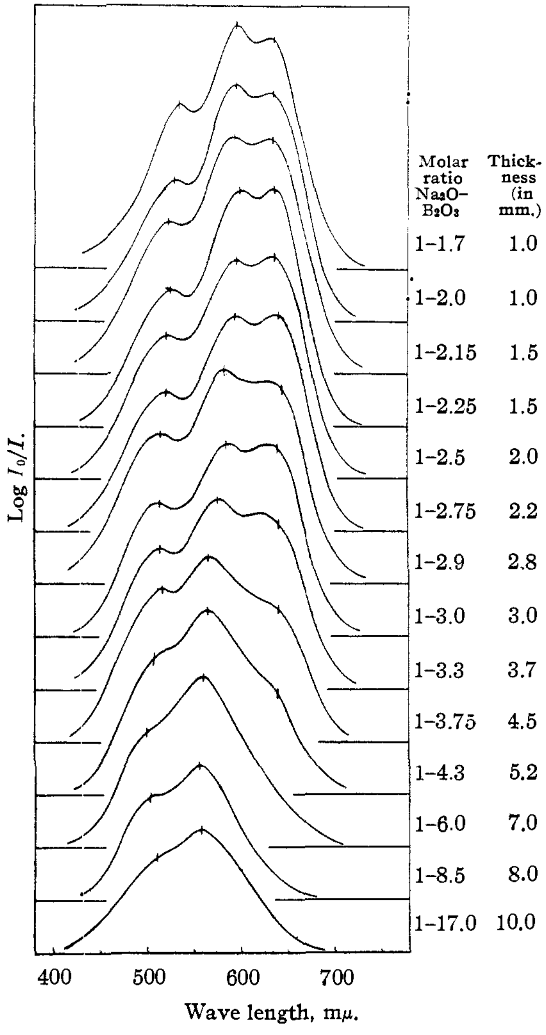

Fig. 2.—The absorption spectra of sodium oxide–boric oxide cobalt glasses. Cobalt concentration = 0.2 g. Co per 100 g. of glass. The sodium oxide–boric oxide molecular ratios and the thickness values in mm. of the samples are given to the right of the curves. It should be noted that a greater thickness or concentration of cobalt is necessary to produce an absorption band in the pink samples with an extinction coefficient of approximately the same value as in the blue samples. In order to avoid the overlapping of curves, the ordinates of each curve in this and subsequent figures in this paper have been offset 0.4 in extinction coefficient (log I_0/I) above each adjacent curve.

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(7) Brode, This Journal, **46**, 581 (1924).

(8) Brode, *Bur. Standards J. Research*, **2**, 520 (1929).

that an intermediate compound or partially coördinated complex must exist between the blue and pink colored forms. A similar intermediate compound was previously shown to exist[5c] between the pyridine–quinoline blue solutions and the halogen acid blue solutions.

With an extremely low concentration of boric oxide, the band at 640 mμ drops slightly in intensity in much the same manner as has been shown in the case of certain indicators with an excess of alkali or acid concentration.

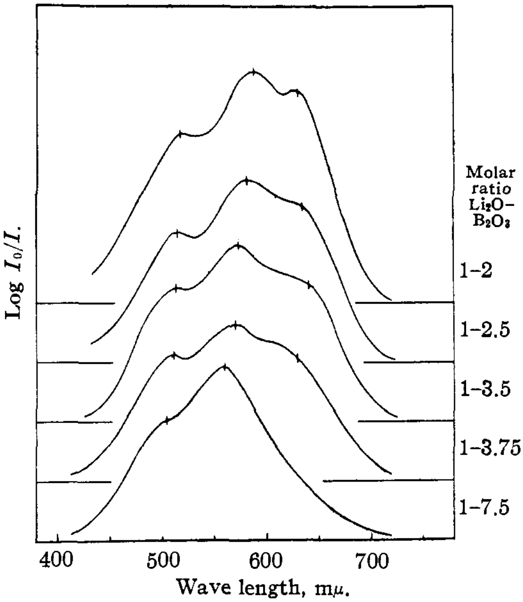

Fig. 3.—The absorption spectra of lithium oxide-boric oxide cobalt glasses. The molar ratios of the components are given to the right of each curve.

The data on the Li, K and Cs glasses (Figs. 3, 4 and 5) are similar to the data on the sodium glasses, although there are some progressive changes on substituting the elements in the order of their periodic arrangement. While lithium glasses have a color change point near that of the sodium glasses, the equilibrium range covers a much wider variation of concentration, so that those with the lowest amount of boric oxide are still a decided purple in color and show a considerable amount of absorption due to the pink or cobaltous color. In general the lithium glasses were high melting and had a strong tendency to crystallize. As would be predicted, the potassium glasses have apparently a smaller range of concentration variation for the color change and hence give a purer blue color with a sharper absorption band in the red than the corresponding sodium and lithium glasses. As in the case of the latter, there is a drop in the intensity of the 640 mμ band with a very low boric oxide concentration. In intermediate concentrations, however, this band is much stronger than the same band in the sodium glasses. In the blue potassium glasses there is a slight shift of the bands toward the red. This is not due to an increase in the molecular weight of the chromophore such as would occur if the potassium were directly combined with the cobalt, but rather to the smaller amount of absorption of the pink band which by its additive effect would cause an apparent shift in the wave length of the band toward the blue. If this shift had been due to an increase in molecular weight, then the bands of the cesium glasses with an atomic weight of about three times that of potassium and nearly six times that of sodium should show a marked shift, just as the shifts in the halogen–cobalt complexes from Cl, to Br, to I are in proportion to their atomic weights.[5b] There was no such shift in the cesium glasses (Fig. 5), which confirms the theory that the cobalt is not directly coördinated with the alkali metals. There is a noticeable variation of the relative intensities of the 640 mμ band in the different alkali oxide glasses. This band is relatively weak in the lithium glasses and strong in the potassium glasses. The cesium glasses indicate a still stronger band at this point but the measurements of their curves were not so accurate as the others. The melting point of (Cs_2O–$3B_2O_3$) glass was rather high and there was a marked tendency to crystallize. In addition, the cesium seemed to absorb oxygen very easily, forming the higher oxides and yielding an opaque glass. The only two satisfactory cesium glasses were the Cs_2O–$2B_2O_3$ and the Cs_2O–$2.5B_2O_3$, the latter being quite low melting.

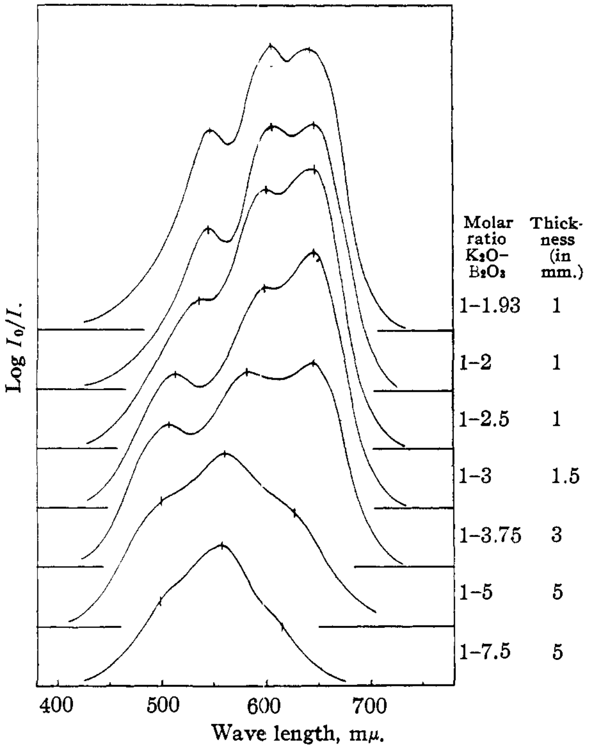

Fig. 4.—The absorption spectra of potassium oxide–boric oxide cobalt glasses. The molar ratios of the components are given to the right of each curve.

If the color is due to an oxide complex, similar to the quinoline halide complex, then it should be possible to convert the oxide complex to a halide complex without passing through the pink or cobaltous stage. Addition of alkali metal halides produced first a purple-gray glass with a flat broad band due to the two component band systems and a possible intermediate halogen–oxygen complex. On further addition of the alkali metal halide the halogen system with bands identical with those obtained in the concentrated halogen acids was obtained.[5b] The chloride glass was bright blue-green, the bromide glass yellow-green and the iodide glass yellow in color. Only a trace of halide was necessary to convert the pink glasses to the corresponding halogen colored glass; the intense alkali blue glasses, however, required considerable halide to convert them to the halogen colors.

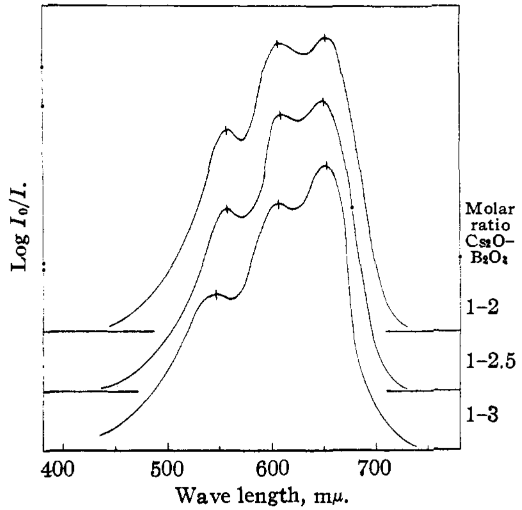

Fig. 5.—The absorption spectra of cesium oxide-boric oxide cobalt glasses. The molar ratios of the components are given to the right of each curve.

Summary

A spectrophotometric study has been made of the alkali oxide–boric oxide cobalt glasses. It has been shown that the position of the absorption bands in the blue glasses is unaltered by a change of alkali oxide and hence the alkali metal itself is not directly attached to or a part of the chromophore. The change of the alkali oxide to the corresponding alkali sulfide or halide produces bands which are characteristic of these complexes and whose frequency position is shifted with a change of the atomic weight of the substituting element. The cobalt oxide blue glasses therefore belong to the same system of coördinated cobalt blue compounds as the halogen acid colors, the halogen salt colors such as cobaltous chloride in the presence of calcium chloride or aluminum chloride, the alcohol, acetone, ether, and other organic blue solutions, the pyridine and quinoline–halogen complexes and the sulfur and thiocyanate colors. In all of these the coördinating element adjacent to the cobalt is apparently part of the chromophore while other elements attached to this element have little influence on the band other than an indirect effect which is apparent in the data only as modifications in the relative intensity of the bands. The pink glasses

containing a high concentration of boric oxide have the same absorption band as is to be found in the water solutions of cobaltous salts or the sulfuric and acetic acid solutions and which is ascribed to the uncoördinated cobaltous atom. It is possible to prepare cobalt glasses with the proper concentration of oxides such that they will be pink at a given temperature and blue at a higher temperature. For this purpose potassium oxide is to be preferred to lithium and sodium oxides. With a given molar concentration, a more brilliant blue glass is obtained with potassium than with sodium or lithium oxides.

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The Solubility of Nitrogen in Water at 50, 75 and 100° from 25 to 1000 Atmospheres

BY R. WIEBE, V. L. GADDY AND CONRAD HEINS, JR.

There is no reliable method by which the solubilities of gases in liquids at high pressure may be calculated or predicted. Carefully compiled experimental data, therefore, become of theoretical as well as immediate practical value.

Goodman and Krase[1] measured the solubility of nitrogen in water from 100 to 300 atmospheres over a wide range of temperatures while Frolich and associates[2] obtained the solubility of nitrogen in water at 25° up to 200 atmospheres. It will be seen that there is some disagreement between the various results. The data presented here are an extension of previous work.[3]

Apparatus and Method

The apparatus and method used are somewhat similar to those described previously.[4] Fig. 1 shows the apparatus. Cylinders A and B of 1000 and 300 cc. capacity, respectively, were filled with water to three-fourths capacity. For the high pressure approach gas was bubbled through A and B successively at a pressure above the final value in order to obtain supersaturation. The pressure was then lowered to the desired level and gas was bubbled through for several hours. The gas flow was then turned off and, after standing from two to fourteen hours, samples were taken. In the low pressure approach the water was saturated at a pressure below the final value and then gas was bubbled through at the final pressure for about three hours. Samples were taken only from B. A was used as a

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[1] Goodman and Krase, *Ind. Eng. Chem.*, **23**, 401 (1931).

[2] Frolich, Tauch, Hogan and Peer, *ibid.*, **23**, 548 (1931).

[3] Wiebe, Gaddy and Heins, *ibid.*, **24**, 927 (1932).

[4] Wiebe, Gaddy and Heins, *ibid.*, **24**, 823 (1932).