mixtures containing 4, 8, 12, and 16 weight % of nitrogen dioxide and 1, 2, 3, 4, and 5 weight % of water (Tables IV and V). The corresponding data for nitric acid (*5*) have been included for comparison.

The interpolation and subsequent smoothing have resulted in a small decrease in the accuracy of the tabulated data over that of the experimental. Nevertheless, the uncertainty in the values of the pressure given in the tables is believed to be less than 5 pounds per square inch or 1%, whichever is the larger value, at temperatures up to 125°C., and V^G/V ratios up to 0.6. The uncertainty may be somewhat larger at the higher temperatures and larger V^G/V ratios, particularly so, for the nitric acid–nitrogen dioxide mixtures.

Figure 5 shows graphically the relations between the equilibrium pressure and the amount of nitrogen dioxide initially present for different values of V^G/V at 85° and 150°C. The decrease in the equilibrium pressure with the amount of nitrogen dioxide added is greatest for small V^G/V ratios. At large V^G/V ratios, the relationship between the equilibrium pressure and the amount of nitrogen dioxide is essentially linear. The slope of these curves at large V^G/V ratios changes from negative to positive with increasing temperature. Between 105° and 125°C. (not shown on the graph) the equilibrium pressure is practically independent of the amount of nitrogen dioxide added. The increase in equilibrium pressure with the amount of nitrogen dioxide added at large V^G/V ratios and at the higher temperatures is indicative of an increase in the partial pressure of nitrogen dioxide relative to that of oxygen in the gas phase.

The relations between the equilibrium pressure and the V^G/V ratio for the nitric acid–water mixtures studied are shown in Figure 6. The decrease in the equilibrium pressure with the amount of water added, on a weight basis, is considerably more pronounced than that obtained by the addition of nitrogen dioxide. However, this difference is much reduced if the comparison is made on a mole basis. The effects of V^G/V and temperature are about the same as for the nitric acid–nitrogen dioxide mixtures, except that the slopes of the curves are all negative for the range of concentration investigated.

Figure 7 shows a comparison of the relations between equilibrium pressure and temperature for pure nitric acid, for an 85 to 15% nitric acid–nitrogen dioxide mixture and for a 95 to 5% nitric acid–water mixture at V^G/V ratios of 0.1, 0.4, and 0.8. The curves demonstrate, in a striking manner, the very great dependence of the equilibrium pressure on the V^G/V ratio and the relatively greater effectiveness of water, as compared with nitrogen dioxide, in the reduction of the equilibrium pressure.

LITERATURE CITED

(1) Corcoran, W. H., Reamer, H. H., Sage, B. H., *Ind. Eng. Chem.* **46,** 2541 (1954).
(2) Duffy, C. H., Corcoran, W. H., Sage, B. H., *Ibid.*, **48,** 431 (1956).
(3) Giauque, W. F., Kemp, J. D., *J. Chem. Phys.* **6,** 40 (1938).
(4) International Critical Tables, Vol. III, p. 23, McGraw-Hill, New York, 1928.
(5) Kay, W. B., Stern, S. A., *Ind. Eng. Chem.* **47,** 1463 (1955).
(6) Stern, S. A., Kay, W. B., *J. Am. Chem. Soc.* **76,** 5353 (1954).
(7) Verhoek, F., Daniels, F., *Ibid.*, **53,** 1250 (1931).

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Vapor-Liquid Equilibria in Tetrahydrofuran-Methanol-Methyl Borate System

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Within the past few years, tetrahydrofuran (tetramethylene oxide) has become increasingly important as a commercial solvent, yet the chemical literature presents little information on the distillation behavior of systems containing tetrahydrofuran. Therefore, the present work was undertaken.

A preliminary investigation of the ternary system, tetrahydrofuran-methanol–methyl borate, gave no indication of the formation of a ternary azeotrope. Instead, it was found that upon fractionation of this system, two binary azeotropes which distill independently are obtained. In the presence of an excess of methanol, the well-known methanol-methyl borate azeotrope (*3*) distills at 54.6° C. until the methyl borate is exhausted. The temperature then rises to 59.1° C. and a methanol-tetrahydrofuran azeotrope distills.

As the behavior of the methanol–methyl borate system has previously been reported, only the two binary systems, methanol-tetrahydrofuran and methyl borate–tetrahydrofuran, are considered in this article.

EXPERIMENTAL

Materials. The tetrahydrofuran used was supplied by Du Pont and was distilled from sodium metal. Absolute methanol, supplied by J. T. Baker, was used without further purification. Methyl borate, obtained from Metal Hydrides, Inc., was distilled immediately before using.

Apparatus. The improved Othmer still (*5*) was used without modification to obtain equilibrium compositions. All distillations were carried out at atmospheric pressure, 740 to 750 mm. The thermometers used in this work were calibrated by observation of the ice point and by comparison with a thermocouple at several temperatures in the range of 0° to 60° C.

Analysis. The samples were analyzed by measuring the index of refraction with a Spencer Abbê refractometer and fitting these points to a previously determined curve of composition *vs.* index of refraction. For this work the refractometer was kept in a controlled-temperature room.

VAPOR-LIQUID EQUILIBRIUM DATA

The vapor-liquid equilibrium data for the two binary systems are shown in the Tables I and II and Figures 1 and 2. The graphs are the conventional $X - Y$ plots on which

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Table I. Methyl Borate-Tetrahydrofuran System

Equil. Temp., ° C.	Mole Fraction Tetrahydrofuran: In liquid x	Mole Fraction Tetrahydrofuran: In vapor y	Activity Coefficients: Methyl Borate	Activity Coefficients: Tetrahydrofuran
66.1	0.255	0.297	0.9971	1.1029
65.7	0.385	0.426	1.0004	1.0624
65.2	0.500	0.533	1.0194	1.0414
65.0	0.603	0.624	1.0409	1.0177
65.0	0.690	0.700	1.0636	0.9976
65.0	0.769	0.773	1.0800	0.9885
65.0	0.814	0.829	1.0105	1.0015
65.0	0.890	0.890	1.0991	0.9834
65.0	0.929	0.931	1.0681	0.9855

Table II. Methanol-Tetrahydrofuran System

Equil. Temp., C.	Mole Fraction Methanol: In liquid x	Mole Fraction Methanol: In vapor y	Activity Coefficients: Methanol	Activity Coefficients: Tetrahydrofuran
60.6	0.173	0.280	1.8678	0.9991
59.4	0.345	0.409	1.4365	1.0792
59.1	0.512	0.500	1.2039	1.2444
59.4	0.654	0.595	1.1072	1.4061
60.0	0.767	0.691	1.0689	1.5591
60.9	0.849	0.760	1.0194	1.8036
61.7	0.897	0.829	1.0207	1.8364
62.6	0.943	0.896	1.0112	1.9556

the points determined experimentally are shown as small circles. The solid curve in each case is the plot of an empirical equation fitted to the experimental points by the method of Prahl (*6*). The activity coefficients given in Tables I and II were calculated from the expression

$$\gamma = yP_T/xP$$

where γ is the activity coefficient, P_T is the total pressure, and P is the vapor pressure of the component under the conditions represented by the x and y values.

Vapor pressure data for methanol and methyl borate are available from the literature (*3, 7*). Vapor pressure data for tetrahydrofuran, obtained from Ernsberger (*2*), determined by the Smith-Menzies isoteniscope method, fit the equation

$$\text{Log } P_{\text{mm.}} = 7.9250 - 1707.3/T$$

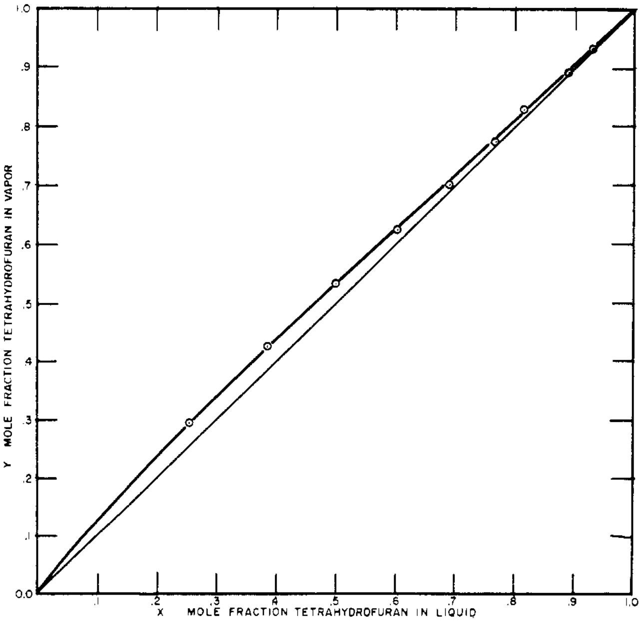

Figure 1. Vapor-liquid equilibrium in the system tetrahydrofuran-methyl borate

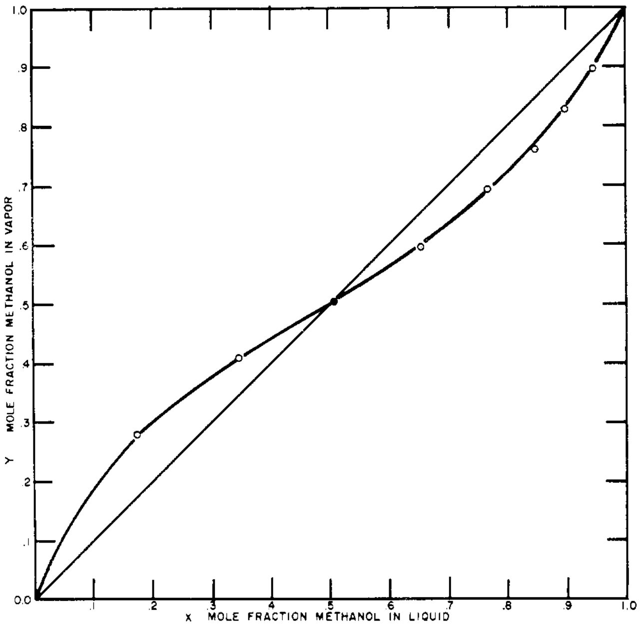

Figure 2. Vapor-liquid equilibrium in the system methanol-tetrahydrofuran

Figure 1 and Table I contain the equilibrium data for the tetrahydrofuran-methyl borate system. No azeotrope formation occurred in this system. The constants of the Prahl equation are

$$A = -496.5$$
$$B = 3.4118$$
$$C = -0.009$$

The vapor-liquid equilibrium data for the system methanol-tetrahydrofuran are shown in Figure 2 and Table II. Azeotrope formation is indicated. The Prahl constants characterizing this system are

$$A = 2.476$$
$$B = 0.386$$
$$C = 0.452$$

After the equilibrium data were obtained from the Othmer still, a mixture was made up as close to the azeotropic composition indicated by Figure 2 as possible. This mixture was fractionally distilled through a packed column and samples drawn off at intervals for analysis. From these analyses, it was determined that the methanol-tetrahydrofuran azeotrope occurs at 50.4 mole % of 31.1 weight % methanol, and distills at 59.1° C. (740 mm.).

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Du Pont de Nemours, E. I., & Co., Inc., tech. bull. quoting unpublished data.
(2) Ernsberger, F. M., unpublished work.
(3) "Handbook of Chemistry and Physics," 37th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1955-56.
(4) Lecat, M., *Rec. trav. chim.* **47**, 13 (1928).
(5) Othmer, D. F., *Ind. Eng. Chem., Anal. Ed.* **4**, 232 (1932).
(6) Prahl, W. H., *Ind. Eng. Chem.* **43**, 1767 (1951).
(7) Webster, S. H., Dennis, L. M., *J. Am. Chem. Soc.* **55**, 3233 (1933).

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