DETERMINATION OF METHANOL IN THE PRESENCE OF ETHYL ALCOHOL

BY

F. S. MORTIMER

Illinois Wesleyan University, Bloomington

INTRODUCTION

Several methods have been proposed for the determination of methanol in the presence of ethyl alcohol and water. Practically all of these methods depend upon the oxidation of the methanol to formaldehyde and the subsequent determination of this substance.

Leach and Lythgoe (J. Amer. Chem. Soc., Vol. 27, p. 964, 1905), however, have proposed a method by which both methyl and ethyl alcohols may be found by a determination of two physical properties. These investigators have pointed out that equal weight concentrations of these two alcohols in water have nearly the same density; hence a determination of the density makes it possible to estimate the total alcoholic content of the mixture. In order to determine the relative amounts of each alcohol present, it was assumed that "addition of methyl to ethyl alcohol decreases the refraction in direct proportion to the amount added."

Leach and Lythgoe gave no data (except the analyses of some synthetic mixtures) for the refraction of ternary mixtures of water methanol, and ethyl alcohol. It was our purpose to determine this data and to attempt thereby to develop a graphical method for the analysis of methyl and ethyl alcohols in the presence of water or, for that matter in the presence of any non-volatile impurity.

It soon become apparent that the results, especially those for refractive index, are much more regular for mixtures containing less than 50 per cent of total alcohol by weight than for those which contain more than this amount. As all mixtures may readily be brought within this range of concentration, only this portion of the system has been investigated.

Procedure

The samples of alcohol used in this investigation were treated to remove impurities, but they were not rendered absolutely dry. The amount of water present was determined and allowance made for it in calculating the concentrations. Two stock solutions, each containing the two alcohols, were made up. Solution I contained 36.68 parts of methyl to 61.32 parts of ethyl and Solution II contained 73.97 parts of methyl to 26.03 parts of ethyl alcohol, the solutions being made up on the weight basis. Appropriate mixtures of each of these stock solutions were then made up with water in small glass-stoppered bottles and the refractivities determined at 20° C. by means of the Zeiss immersion refractometer using the standard procedure. Two other solutions, one containing 50 per cent by weight of methanol in water and the other 50 per cent by weight of ethanol in water were also prepared. As the densities of these two liquids are nearly the same, appropriate mixtures were made up on a volume basis and the refractivities read as before. The results for all mixtures are shown in Table I.

Table I

Refractivities of Ternary Mixtures of Methyl and Ethyl Alcohols With Water

Solution I		Solution II		Solutions III and IV		
Total % Alcohol	Scale reading	Total % Alcohol	Scale reading	Parts 50% Methanol	Parts 50% Ethanol	Scale Reading
0.0	14.5	0.0	14.5	100.	0.	39.8
		4.62	18.0	90.	10.	45.0
4.26	19.1	8.85	21.7	80.	20.	50.2
6.93	22.6	16.25	28.4	70.	30.	55.7
13.3	31.1	22.6	34.8	60.	40.	60.9
16.5	35.7	27.95	39.6	50.	50.	66.0
26.5	50.0	36.8	46.0	40.	60.	71.0
34.1	59.3			30.	70.	76.1
45.7	68.5			20.	80.	81.1
				10.	90.	86.0
				0.	100.	90.8

These results together with the results of Leach and Lythgoe for the pure alcohols, were plotted to a large scale and the concentrations for even refractometer scale readings were read off and used in plotting the ternary diagram shown in figure 1. It will be noted from this diagram that the lines of equal refraction, although nearly straight, are not quite parallel. Neither are they equally spaced. This last condition, at least, would have to obtain in order for the method of Leach and Lythgoe to give exact results in the analysis of samples containing methanol. However, with the density and refractivity determined, it is not difficult to find from the ternary diagram the relative amounts of each of the three substances present in the mixture, provided, of course, that there are not more than traces of other volatile substances present to interfere.

We have found however, that a method of "factors" may be used by which it is possible to calculate very closely the percentages of methanol and ethanol present without the bother of constructing and interpolating from the ternary diagram.

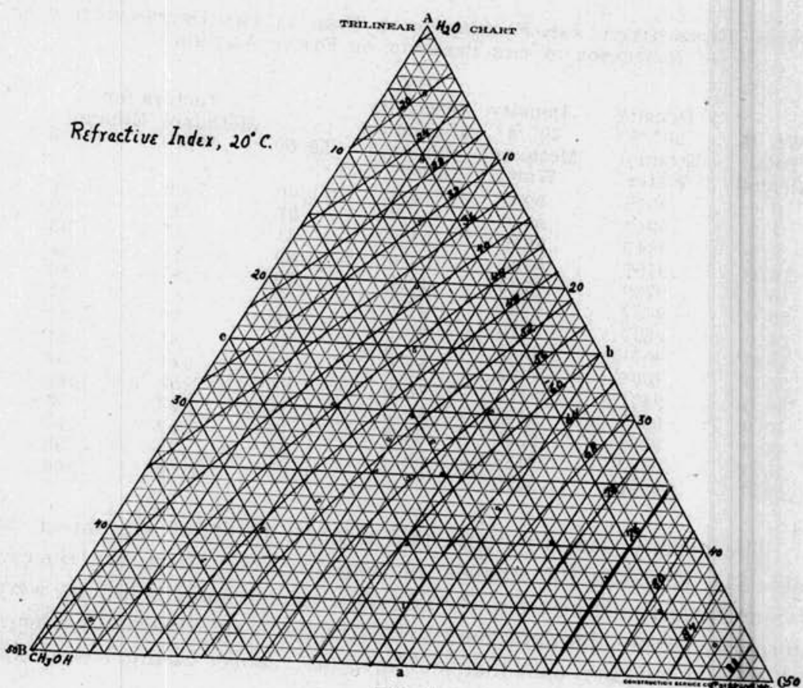

FIG. 1

Following are the steps in this method: (1) obtain the refractometer reading at 20° C. and the density at 20°/4°; (2) using the density tables for ethyl alcohol-water, find the weight per cent of total alcohol present in the solution; (3) with this per cent of alcohol find what would be the refractometer reading if ethanol were the only alcohol present; (4) subtract the actual refractometer reading found in (1); (5) multiply this difference by the appropriate factor and the product will represent the per cent of methanol present in the sample. The factor to be used is found in Table II after that number which represents the total per cent of alcohol in the sample as found from the density. The factor to be used first is that one in which it is assumed that not over one-half of the total alcohol is methanol, viz. column 5. If after multiplying, it turns out that the ratio of methanol to ethanol is greater than 1 to 1 (this is seldom the case) then it is possible to make another estimate from the data of Table II and obtain a more appropriate factor. To facilitate its use, all of the data of Table II should be plotted on one graph, using per cent alcohol as one of the co-ordinates.

TABLE II

DENSITY, REFRACTIVITY AND FACTORS TO BE USED IN THE DETERMINATION OF METHANOL IN THE PRESENCE OF ETHYL ALCOHOL

Wt. % Total Alcohol	Density 20°/4° Ethanol-Water	Density 20°/4° Methanol-Water	Refractivity of Ethanol-Water at20°	Factors for Methanol/Ethanol 50/50	80/20	100/0
0.0	.9982	.9982	14.5	1.00	1.00	1.00
4.0	.9910	.9910	20.7	.87	.92	.96
8.0	.9847	.9845	27.8	.81	.87	.92
12.0	.9791	.9784	35.0	.80	.84	.88
16.0	.9739	.9726	42.5	.795	.82	.86
20.0	.9687	.9667	50.5	.79	.81	.83
24.0	.9632	.9610	58.2	.79	.80	.81
28.0	.9571	.9549	65.5	.80	.81	.81
32.0	.9504	.9485	71.7	.83	.84	.84
36.0	.9431	.9416	76.9	.88	.88	.88
40.0	.9352	.9345	81.3	.93	.93	.93
44.0	.9269	.9268	85.2	.98	.97	.97
48.0	.9183	.9183	88.7	1.00	.99	.99
52.0	.9099	.9099	91.8	1.01	1.00	1.00

The density data for these two alcohols in water are shown in Table II. The data for ethanol solutions are taken from the Bureau of Standards Bulletin 9, No. 3. The data for methanol solutions were interpolated from the data summarized in the Van Nostrand's Chemical Annual together with that of Hertz (Z. Anorg. Chem. 104, p. 47, 1918).

TABLE III

	% Total alcohol	Refractivity observed	Refractivity from ethanol curve	Dif.	Factor	Product = % methonal	Methanol As made	Methanol Found by L. & L.
1.	47.41	51.9	88.1	36.2	.99	35.8	35.56	35.42
2.	43.43	62.4	84.7	22.3	.97	21.6	21.71	21.38
3.	25.64	34.2	61.25	24.05	.80	19.2	19.23	19.76
4.	48.86	77.5	89.3	11.8	1.00	11.8	12.21	11.77
5.	17.00	34.0	44.75	10.75	.79	8.5	8.5	8.92
6.	23.92	50.2	58.0	7.8	.79	6.15	5.98	6.48

In order to test this method of analysis we have made up a number of synthetic mixtures of known composition and in every case the methanol found was within a small fraction of 1 per cent of that known to be present. Table III shows results of tests on some synthetic mixtures made by Leach and Lythgoe (op. cit.) and which they used to illustrate their method of analysis. We have recalculated these results by the method here outlined and the values are shown in the table.

It will be observed that with one exception the results as calculated by the method outlined above actually give more nearly the correct per cent of methanol than does the original method of Leach and Lythgoe.