

Vapor Liquid Equilibrium and Refractive Indices of the Methanol-Ethylene Glycol System

TERRY H. BAKER, GERALD T. FISHER, and JOHN A. ROTH
Vanderbilt University, Nashville, Tenn.

The equilibrium data of the system at 760 mm. of Hg is reported. Slight deviations from Raoult's Law were observed. The refractive indices at 13° C. are reported.

ALTHOUGH THE SEPARATION from binary mixtures of methanol and ethylene glycol has been performed commercially for years, there are no reported equilibrium data on the system. These data have now been determined.

EXPERIMENTAL

A modified Othmer still (1) was used to determine the equilibrium data. Reagent grade (Fisher Scientific Company) materials were used as standards and in the distillation. A Bausch and Lomb 33-45-03-01 precision refractometer was used for the analyses. The refractive indices were measured at 13.0° C. because the lower limit of the refractometer was above the refractive index of methanol at 25° C.; lowering the temperature to 13° C. raised the refractive index sufficiently to enable the particular set of prisms available to be used. The literature values of the refractive indices of methanol and of glycol, corrected to 13° C. (2), are 1.3309 and 1.4339. The values experimentally determined for the pure materials are 1.3308 and 1.4333. The values indicate that the reagent grade chemicals were of high purity. The pressure was controlled at 760 ± 1 mm. of Hg by a positive air bleed through a Cartesian Manostat. The temperatures were measured with a thermometer of 0° to 360° C. range, calibrated in 1° C. intervals.

RESULTS

The refractive indices at 13.0° C. of the system are given in Figure 1 and in Table I. The composition-temperature

data are in Figures 2 and 3 and in Table II. The equilibrium diagrams calculated from vapor pressure data (2) and from Raoult's Law are shown as dotted lines in Figures 2 and 3.

DISCUSSION

Some difficulty was encountered in the measurements. The material returning to the boiler from the condenser formed bubbles before reaching the heater surface because the bubble point of the condensed vapor was so much lower than the temperature of the liquid in the still. This caused an instability in the observed temperature. None of the standard modifications of the Othmer still prevented this instability.

Table I. Refractive Indices of Methanol-Glycol Solutions at 13.0° C.

| Mole Fraction Methanol | Refractive Index at 13° C. |
|------------------------|----------------------------|
| 0.0000 | 1.43325 |
| 0.1131 | 1.42605 |
| 0.2141 | 1.41928 |
| 0.3799 | 1.40629 |
| 0.4054 | 1.40427 |
| 0.6032 | 1.38494 |
| 0.6679 | 1.37768 |
| 0.8051 | 1.36071 |
| 1.0000 | 1.33084 |

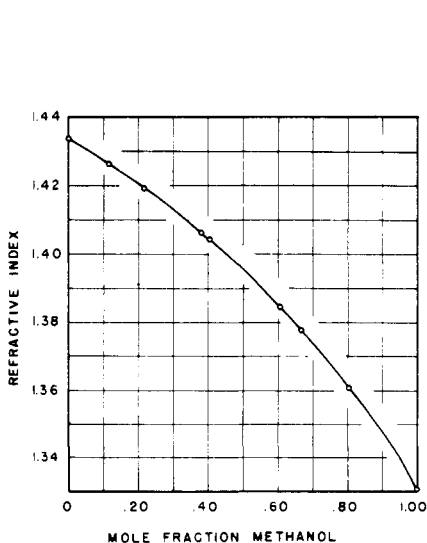


Figure 1. Refractive indices (13° C.) of methanol-glycol

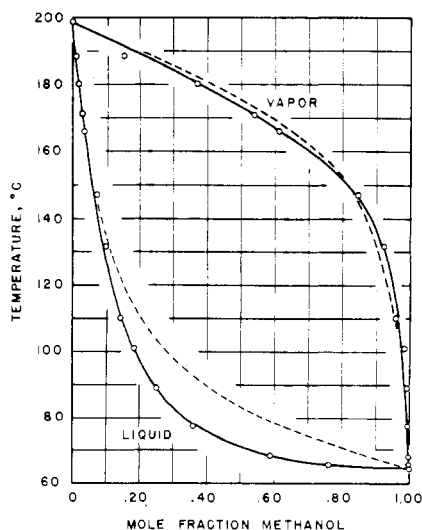


Figure 2. Dew point-bubble point diagram of methanol-glycol at 760 mm. of Hg

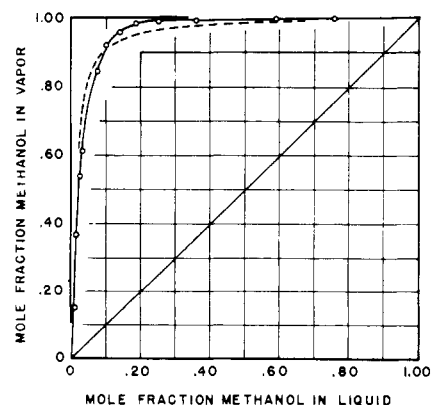


Figure 3. Vapor-liquid equilibrium of methanol-glycol at 760 mm. of Hg

Table II. Equilibrium Data

| Temp., °C. | Refractive Index | | Mole Fraction Methanol | |
|---------------|------------------|---------|------------------------|-------|
| | Liquid | Vapor | Liquid | Vapor |
| 64.1 | ... | ... | 1.000 | 1.000 |
| 65.5 | 1.36761 | 1.33103 | 0.754 | 0.999 |
| 68.0 | 1.38677 | 1.33421 | 0.590 | 0.998 |
| 77.5 | 1.40824 | 1.33175 | 0.360 | 0.995 |
| 89.2 | 1.41712 | 1.33135 | 0.250 | 0.995 |
| 101.0 | 1.42131 | 1.33382 | 0.185 | 0.985 |
| 110.0 | 1.42426 | 1.33853 | 0.142 | 0.960 |
| 131.5 | 1.42719 | 1.34424 | 0.100 | 0.922 |
| 147.2 | 1.42914 | 1.35597 | 0.075 | 0.845 |
| 166.0 | 1.43137 | 1.38433 | 0.032 | 0.610 |
| 171.1 | 1.43172 | 1.39182 | 0.027 | 0.540 |
| 180.3 | 1.43240 | 1.40748 | 0.015 | 0.368 |
| 188.6 | 1.43273 | 1.42363 | 0.010 | 0.152 |
| 199.0 | ... | ... | 0.000 | 0.000 |

The activity coefficients, $\gamma = (y/x)/(p^0/p)$, were calculated but are not reported. The nature of the system is such that one of the phase compositions is within 0.02 mole fraction of a pure material for nearly all points. Any normal experimental error in composition determination causes exaggerated errors in the activity coefficients. It was felt that the comparison of the data with that calculated from Raoult's Law is more significant.

LITERATURE CITED

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Vapor-Liquid Equilibria for the Methyl Oleate and Methyl Stearate Binary System

ARTHUR ROSE and VERLE N. SCHRODT¹

The Pennsylvania State University, University Park, Pa.

The methyl oleate-methyl stearate vapor-liquid equilibrium behavior deviates only slightly from the ideal. The total pressure technique, using a modified U-tube manometer, gave precise vapor pressure measurements.

PRECISE DETERMINATIONS of the vapor pressures of pure methyl oleate and methyl stearate and of known mixtures of these compounds have revealed that the system exhibits nearly but not quite ideal vapor-liquid equilibrium behavior. The nonidealities are negative deviations from Raoult's law. The equilibrium data reported here are in qualitative agreement with gas chromatographic behavior of these compounds. A binary mixture of methyl oleate and methyl stearate separates normally in gas chromatography on a saturated hydrocarbon substrate, but on a polyester substrate, a reversal of volatility occurs because of interaction of the oleate double bond with ester groups.

The equilibrium data were obtained by the total pressure technique. A special adaptation of an ordinary U-tube manometer was used to make the precise pressure measurements that were necessary in order to reveal the slight nonidealities present in the methyl oleate-methyl stearate system. The relative volatility α , defined as the ratio of the vapor pressures of the pure components, ranges from about 1.08 to 1.15.

EXPERIMENTAL

The need for high precision can be appreciated by plotting values of y - x vs. x for the actual nonideal system and for

¹ Present address: Monsanto Chemical Co., St. Louis 66, Mo.

the same system assuming ideal behavior and also for a system which has a larger separation factor. This is shown in Figure 1. To define differences due to nonideal behavior in the oleate-stearate system, analytical techniques sensitive to 0.1% or better are required. It is difficult or impossible to achieve this on rather small samples. However, quite precise measurements of the vapor pressures can be made and this was a main reason for using the total pressure approach.

Apparatus. A U-tube manometer, suitably modified, was used successfully to measure the low pressure-high temperature equilibrium pressures. A drawing of the manometer is shown in Figure 2. The problems which arise in low pressure-high temperature work with organic materials prevented the use of presently available equilibrium stills.

Successful precise equilibrium measurements in the range 30 to 700 mm. of Hg pressure on fatty acids, esters, and alcohols in this laboratory were first made (9) using a Cottrell-type equilibrium still developed by Williams (11). Sumantri (15) and Supina (10) determined that this type of unit had an upper operating limit with fatty acids and esters of about 180°C. and a lower limit at 20 to 30 mm. of Hg. In the region below 20 mm. of Hg, the pressure drop through the Cottrell tube may account for three or more centigrade degrees of superheating, thus limiting the usefulness of this type of still for low pressure measure-