

Distribution of Benzene in the Diethyl Ether—Magnesium Bromide System at 25°C.

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It is a well established fact that magnesium bromide with excess diethyl ether forms two conjugate liquid phases at 25°C., the upper layer consisting of ether saturated with about 3% magnesium bromide, the bottom layer containing about 39% magnesium bromide. On cooling below 32°C., solid crystalline etherates of magnesium bromide can be obtained (2, 3). A recent study by one of the authors (4) on the preparation of anhydrous magnesium bromide in diethyl ether indicated that the presence of benzene tended to increase the miscibility of the two conjugate liquids. Its presence also tended to increase the solubility of the etherate crystals at lower temperatures. A study of the distribution of benzene in the two-layer diethyl ether—magnesium bromide system at 25°C. has now been made.

EXPERIMENTAL

A typical procedure involved the preparation of anhydrous magnesium bromide (4) which was redissolved in sufficient reagent grade diethyl ether to form about 40 ml. of the two-layer system. In order to have a sufficient working depth in each of the two partially miscible liquids, the conjugate system was placed in a 50 ml., glass stoppered graduated cylinder. The cylinder holding the liquids was immersed in a constant temperature water bath at 25°C. in such a way that the level of liquid in the cylinder was well below the water level.

Samples were removed from each layer, weighed and analyzed for bromine. Approximately 2 ml. of reagent grade benzene was then added and allowed to stand from 5 to 15 hours with frequent shaking to insure equilibrium conditions. After allowing for complete separation of the two liquids, samples were removed from each layer and analyzed for bromine and benzene. Separate samples were used for the analysis of each component. Several check analyses indicated that equilibrium was reached in less than five hours. An additional 2 ml. of benzene was then added to the system and, after attainment of equilibrium, further analyses were made. This procedure was repeated until the two layers became completely miscible at 25°C. Precautions, such as oven dried apparatus and extensive use of calcium chloride drying tubes, were taken at all times to insure anhydrous conditions, since small amounts of water are known to influence the system (3, 5).

ANALYSIS. Due to the high volatility of the liquids, a weighing pipet of special design was devised from 8 mm. soft glass tubing. The pipet was made by drawing the glass, on each side of a section about 4 cm. in length, to a long tapered capillary. These capillaries had two right angle bends to facilitate holding the sample while the ends were sealed in a small flame. The bulb of the pipet, which had a capacity of 1 to 2 ml., was covered with a piece of surgical gauze saturated with chloroform during the sampling and sealing of the ends. The rapid evaporation of the chloroform lowered the volatility of the sample to a point where loss by evaporation was negligible. After weighing, one of the curved tips was broken beneath the surface of the liquid necessary for the analysis. The upper tip was then broken and the contents of the pipet were transferred quantitatively to the liquid. Water was used for the determination of magnesium bromide and isooctane for benzene.

Bromine was determined by the standard Volhard procedure using solutions of standard silver nitrate and potassium thiocyanate with ferric alum as an indicator.

Since no simple, reliable procedure for the determination of diethyl ether was found, it was decided to determine the amount of benzene in each sample. One of the fundamental properties of double bond linkage in organic compounds is their ability to absorb electromagnetic vibrations in the wave length range of the ultra-violet. In his study of hydrocarbon-type hydrates, Whalen (6) had successfully determined the amount of toluene in chloroform by the absorption of ultra-violet. This method was used for the determination of benzene, which also shows appreciable absorption in the near ultra-violet (1).

Preliminary investigation showed the necessity of a high degree of dilution for the benzene in order for absorption readings to be made. Isooctane (3, 3, 4-trimethylpentane) of spectrophotometric grade was found to have no absorption in the ultra-violet range used in these determinations and served as a very satisfactory diluent.

Examination of the absorption spectrum of benzene revealed a high peak between 252 and 256 $m\mu$. Further close examination of this range, using solutions of benzene in isooctane, indicated that a wave length range from 254.50 $m\mu$ to 254.75 $m\mu$ could be used for analytical purposes. A Beckman Model DU Spectrophotometer with silica cells and a slit width of 0.4 mm. was the instrument used.

Solutions of benzene and diethyl ether of known weight composition were prepared. One milliliter of each of these solutions was diluted 1 to 1000 with isooctane and the absorption measured. Diethyl ether had no

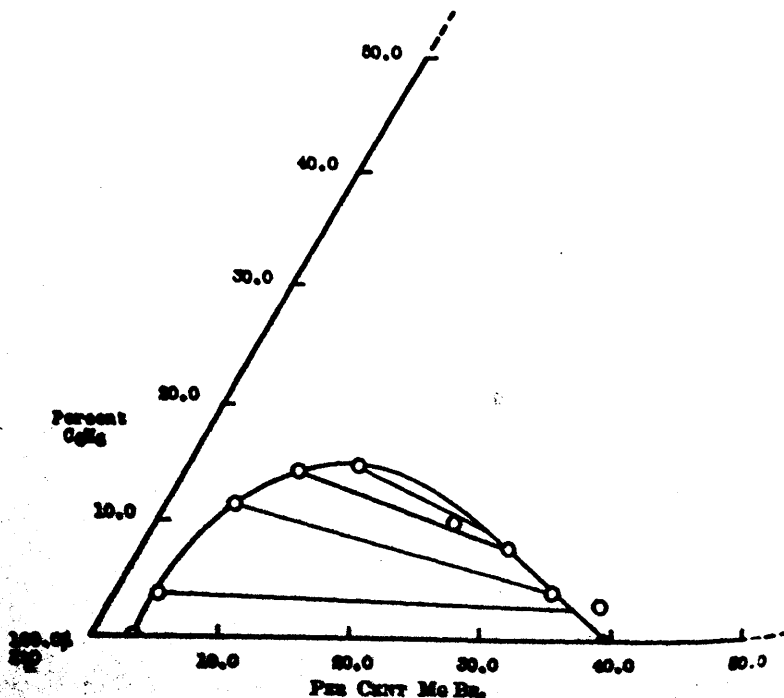


FIGURE 1. Benzene-Diethyl Ether-Magnesium Bromide System at 2°C.

absorption in the ultra-violet range used. From these data a working curve was obtained by plotting absorption values against the number of grams of benzene per liter of solution. Beer's law was found to hold up to 0.05% benzene in the diluted solutions or 50% benzene in the original sample.

Samples of each of the two liquid layers were taken after each addition of benzene to the system as described above. The weighed sample was transferred quantitatively to a 10 ml. volumetric flask containing some isooctane and then diluted to volume. The magnesium bromide, being insoluble in isooctane, precipitated out at this point. After thorough mixing of the sample and the isooctane, the precipitate was allowed to settle. One milliliter of the clear solution was diluted 1 to 1000 with isooctane and the absorption measured on the spectrophotometer. The weight of benzene in the original sample could be determined directly from the working curve. Several duplicate determinations, both on samples and on solutions of known composition, checked each other to less than 0.1% benzene by weight.

DISCUSSION AND RESULTS

The results of the analyses for the two-layer diethyl ether—magnesium bromide—benzene system at 25° C. and atmospheric pressure are shown on the partial three-component diagram, Figure 1. Three independent systems were analyzed, but for clarity only one set of data is indicated on the diagram. The values for the light or upper layer followed the curve within $\pm 0.1\%$ by weight. The values for the more viscous bottom layer averaged $\pm 0.5\%$ from the smoothed curve.

The greater deviation for the points richer in magnesium bromide is probably caused by the greater viscosity of the bottom layer. In filling the sampling pipets, previous to sealing them, more of the heavier liquid clung to the walls of the capillary tubes than when the lighter upper layer was being analyzed. In heating the capillary tubes to draw and seal them, a greater error was introduced because of evaporation of benzene and diethyl ether clinging to the sides. Though all the composition points for the bottom layer do not lie on a smooth curve, its direction and relation to the composition of the upper layer is clearly indicated.

The maximum on the binodal curve in Figure 1 indicates that the maximum amount of benzene necessary to render the two-layer liquid system completely miscible is about 15% benzene by weight. This is considerably less than the approximate value of 29% by weight of benzene previously reported in an earlier investigation (4).

As is typical of this type of ternary partially miscible liquid pairs, the apparent maximum on the solubility curve is not necessarily the critical or consolute point where the two liquid phases have identical composition. One system investigated had a total magnesium bromide: diethyl ether ratio of 23:77. Slightly below the point where addition of more benzene would cause complete miscibility, the volumes of the two layers were as nearly equal as could be determined in the graduated cylinder holding the sample. This would indicate that this particular system passed very near the consolute point. This fact, together with careful examination of Figure 1 was utilized in determining the consolute composition.

TABLE I

Analytical Results

SAMPLE	Wt.% MgBr ₂	Wt.% C ₆ H ₆	Wt.% Et ₂ O
A	3.2	—	96.8
B	39.5	—	60.5
A	3.4	3.7	92.9
B	35.5	3.0	61.5
A	5.5	11.6	82.9
B	33.5	4.5	62.0
A	9.0	14.6	76.4
B	23.5	8.0	63.5
A	13.3	15.0	71.7
B	26.0	9.5	64.5
Consolute Point	20±1	13±1	67±1

A refers to the light or upper layer, values $\pm 0.1\%$

B refers to the more viscous bottom layer, values $\pm 0.5\%$

Numerical values, taken from the smoothed binodal curve and expressed in weight per cent are listed in Table I. The weight per cent of diethyl ether was obtained by difference. The critical composition is shown to be about 20% magnesium bromide, 13% benzene and 67% diethyl ether.

The analytical data obtained for the binary two-layer diethyl ether—magnesium bromide system were found to be 3.2% magnesium bromide for the light upper layer and 39.5% magnesium bromide for the heavy bottom layer. These values agree very well with previously determined values of 3.12% and approximately 39% magnesium bromide (3).

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