
THE DISTRIBUTION OF MAGNESIUM BROMIDE IN THE DIETHYL ETHER-WATER SYSTEM AT 25° C

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The distribution of a dissolved substance between two liquid phases was first studied in detail by Berthelot and Jungfleisch (1) who investigated the partition of iodine between carbon disulphide and water. Since that time, hundreds of distribution systems have been more or less thoroughly studied and reported. In a continuing study of the magnesium bromide-diethyl ether system (8-12) it became necessary to know the solubility relationships of magnesium bromide in the conjugate diethyl ether-water system at 25°C. Since these data could not be found in the literature, they were determined in this laboratory.

EXPERIMENTAL

In the study of a three component system, four variables must be considered: pressure, temperature, and the concentrations of at least two components. For a condensed system consisting of solids and liquids, the pressure variable has little effect so the system can be studied at atmospheric pressure without serious error. The temperature variable effects the solubility relationships so it is necessary to maintain a constant temperature.

The choice of analytical methods for the magnesium bromide-diethyl ether-water system was difficult. The quantitative determination of magnesium bromide is relatively simple using the standard Volhard silver nitrate-thiocyanate titration. However, the choice of an analytical method for the other components required considerable investigation. A search of the literature revealed no simple, reliable method for the quantitative determination of diethyl ether. Many methods for the quantitative determination of water were found but few of them were applicable to the system being studied. The Karl Fischer (3) method for the determination of water (7) was adopted for this investigation.

The Karl Fischer reagent was prepared in the usual manner by adding 64 gm. of sulfur dioxide to 269 ml. of cooled pyridine, diluting to one liter with anhydrous methanol and adding resublimed iodine in small amounts until 84.7 gm. of iodine were present. The methanol-water standard solution, for use with the Karl Fischer reagent, was prepared from absolute reagent methanol and distilled water. The water was added with a graduated cylinder to obtain the approximate concentration of 2 to 4 mg. of water per milliliter of solution. After preparation, each solution was allowed to stand for twenty-four hours before being standardized.

To standardize the methanol-water solution, a measured amount of Karl Fischer reagent was titrated with a measured amount of methanol-water solution and the solution ratio, *R*, obtained for the methanol-water solution/Karl Fischer reagent. For precise work, the electrolytic dead stop end point method (14) was found to be most satisfactory, using a magnetic stirrer with glass enclosed iron bar placed in the bottom of the titration flask for agitation. A measured amount of Karl Fischer reagent was added to the titration flask and a weighed amount of water, W, was added using a medicine dropper as the weighing pipet. Excess Karl Fischer reagent was then added to make the total volume of the reagent, *A*. The excess was back titrated with a volume, *B*, of the methanol-water solution. The calculation formula for the titer, *T*, of the methanol-water solution is as follows:

$$\frac{W}{RA - B} = T$$

When analyzing a sample for water, it was found that more precise results were obtained if the sample was added to a measured excess volume of the Karl Fischer reagent. The excess Karl Fischer reagent was titrated with the methanol-water standard solution. The calculation formula for the weight of water, *W*, in the sample is as follows:

$$(RA - B)\,T = W$$

the symbols having the same meaning as defined above.

Even using normal precautions to protect the solutions, for precise work it was found necessary to obtain a new solution ratio, *R*, between the methanol-water solution and the Karl Fischer reagent every hour and a half. The standard methanol-water solution was also restandardized against pure water every few days.

The diethyl ether-water systems were prepared from Merck's absolute reagent diethyl ether, which had been purified by distilling from freshly cut sodium onto freshly cut sodium, and water distilled from a dilute potassium permanganate solution. The Baker and Adamson reagent grade magnesium bromide hexahydrate was used for the magnesium bromide. No special purification was found necessary.

All systems were prepared in a wide-mouthed glass tube 4 cm. by 20 cm. fitted with an outside ground glass cap carrying a mercury seal stirrer. The motor-driven stirrer had two agitators at different levels to insure thorough stirring and true equilibrium conditions. The tube containing the system was immersed at least 15 cm. in a water bath thermostatically controlled at 25.00° ± 0.05°C as measured by a calibrated thermometer.

Special weighing pipettes, ranging in size from approximately 0.5 ml. to 15 ml. capacity were made from soft glass tubing. One end was drawn down to a thin-walled capillary tubing about one millimeter or less in diameter which could be sealed easily in a Tirrill burner flame. The other end was shrunk to fit in a pipette rubber bulb. When properly sealed, these pipettes showed no detectable loss of sample over a one hour period.

The diethyl ether-water-magnesium bromide systems were prepared by adding varying amounts of magnesium bromide hexahydrate to 20 ml. of distilled water and pouring in approximately 100 ml. of diethyl ether. The system was stirred for a minimum of eight hours at constant temperature and allowed to stand for an additional hour before removal of samples.

A desired volume of sample was drawn into the weighed pipette and removed from the system. While drawing air slowly into the pipette, to prevent excessive loss of sample, the tip of the pipette was sealed in a Tirrill burner. After weighing, the tip of the pipette was placed below the surface of the excess Karl Fischer reagent, when water content was being determined, or below the surface of water acidified with nitric acid, when a bromide analysis was desired. The tip was then crushed with a pair of micro-crucible tongs and the inside of the pipette rinsed several times to remove the sample.

It was necessary to cool the barrel of the pipette with shaved ice and to wipe dry immediately before taking the sample. This lowered the vapor pressure of the diethyl ether and limited the loss of sample. To avoid contamination of the bottom or water layer, as the pipette was removed from the system some of the sample was slowly discharged until the pipette was out of the system. The tip of the pipette was wiped dry with a piece of absorbent tissue and sealed in a flame.

The analysis of the water layer for bromide presented no special difficulties. However, the diethyl ether layer contained such a small amount of magnesium bromide, even when in equilibrium with solid magnesium bromide hexahydrate, that its value could not be determined by titration with 0.027 N silver nitrate solution. An attempt was made to approximate the actual concentration of magnesium bromide in the diethyl ether layer.

A relatively large sample, approximately 15 gm. of the diethyl ether layer, was added to 50 ml. of distilled water and the diethyl ether allowed to evaporate. Any magnesium bromide present in the original sample would dissolve in the water as the diethyl ether evaporated. Five milliliters of 0.027 N silver nitrate, with a titer of 5.00 mg. of magnesium bromide per milliliter of solution, were added to the water. No visible precipitate of silver bromide could be seen. There was a possibility of a very faint turbidity. As a comparison, 0.1 ml. of 0.027 N potassium bromide, having a titer of 5.00 mg. of magnesium bromide per milliliter of solution, was added to 50 ml. of distilled water. This solution had a bromide concentration equivalent to 0.0033 per cent of magnesium bromide in a 15 g. sample. Five milliliters of 0.027 N silver nitrate were added to the solution and a very noticeable precipitate of silver bromide was observed.

A number of systems, ranging from diethyl ether and water with no magnesium bromide to a conjugate liquid system in equilibrium with solid magnesium bromide hexahydrate, were prepared and analyzed. A minimum of two independent samples was analyzed for each liquid layer. Average results, expressed in weight per cent, for the two and three phase systems are given in Table I. The values for diethyl ether were obtained by difference. The deviation of individual results from the average was less than 10 parts per 1000.

TABLE I

Distribution at 25°C $MgBr_2$—H_2O—Et_2O

AQUEOUS PHASE				ETHER PHASE		
$MgBr_2$ %	Et_2O %	H_2O %		$MgBr_2$ %	Et_2O %	H_2O %
0.00	6.56	93.44		0.00	98.53	1.47
4.30	4.57	91.13		trace	98.76	1.24
9.90	4.24	85.85		trace	98.78	1.22
25.23	1.95	72.82		trace	99.04	0.96
36.40	0.49	63.21		trace	99.30	0.70
50.01	0.83	49.16	(Sat'd)	trace	99.73	0.27

DISCUSSION

Referring to Table I, it is noted that the presence of a third component, in this case magnesium bromide, alters the mutual solubility of diethyl ether and water. It is a well known fact that, if the third component is considerably more soluble in one solvent, it will decrease the mutual solubility of the two liquids. This is the well known "salting out" effect utilized in many preparations of organic compounds. The data in Table I show that the presence of solid magnesium bromide in equilibrium with a conjugate system of diethyl ether and water decreases the solubility of ether in water from 6.56% to less than 1%; at the same time, the solubility of water in the diethyl ether decreases from 1.47% to less than 0.3%.

The rather unusual character of this system is that there is practically no distribution of magnesium bromide between the water and diethyl ether layers. Even when the solid magnesium bromide is in equilibrium with the liquids and the water layer is saturated at about 50% magnesium bromide, the amount of magnesium bromide in the diethyl ether layer is considerably less than 0.003%.

This situation would not be particularly remarkable if the magnesium bromide were insoluble in anhydrous diethyl ether. However, such is not the case. Anhydrous magnesium bromide is not only soluble in anhydrous diethyl ether but forms a rather unusual binary system consisting of unsaturated solutions up to about 3% magnesium bromide, a two layer conjugate system in which the composition of the lower layer is about 40% magnesium bromide, and two possible solid solvates, the di-etherate and mono-etherate. (6; 8-12). In addition, the hexahydrate of magnesium bromide can exist in stable equilibrium with the conjugate diethyl ether layers at 25°C (11). Thus the lack of distribution of magnesium bromide between the conjugate water and diethyl ether layers is quite interesting.

Equally extreme results have been found by Schuncke (13), who noted that hydrogen chloride leaves diethyl ether completely and passes wholly into water, and by Hill (4, 5) who studied the distribution of silver perchlorate in the benzene-water system and in the water-aniline system. In the first case, the salt passes wholly into the water layer and wholly into the aniline in the second case.

In cases of this type, it is postulated that there can be no molecular species common to both phases. Some properties of magnesium bromide in water solution compared to its properties in diethyl ether solutions support this belief. The electrical conductivity of aqueous magnesium bromide solutions is quite high and the freezing points of these solutions are abnormally low. This indicates rather extensive dissociation into ions. On the other hand, the specific conductivity of anhydrous magnesium bromide in diethyl ether is of the order of 2×10^{-5} mhos (2) indicating relatively few simple ions. Further, a rough determination of the molecular weight of magnesium bromide in diethyl ether solution from vapor pressure lowering (10) gives an approximate value of 225 as compared to 184.2 for the formula weight. This would indicate that, in diethyl ether solution, the magnesium bromide is associated into larger molecules to some extent rather than dissociated as in water solution.

CONCLUSIONS

On a theoretical basis, the distribution law is limited to dilute systems. In the magnesium bromide-water-diethyl ether system, the concentration of the water layer can reach a maximum of about 50% by weight of magnesium bromide.

Also, the two liquid phases shall not change their mutual solubility with change in the concentration of the distributed phase. In the present system, the mutual solubility of water and diethyl ether is greatly decreased.

Further, correction must be made for dissociation, association or chemical combination in either phase. With all three of these phenomena occurring in the magnesium bromide-water-diethyl ether system, it is not surprising that distribution of the magnesium bromide between the two layers could not be detected.

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